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3e COLLOQUE SUR LES SUBSTANCES TOXIQUES

3rd CONFERENCE ON TOXIC SUBSTANCES

88-03825/

PROCEEDINGS

COMPTES RENDUS

3rd Conference on Toxic Substances

3e Conférence sur les substances toxiques

April 6-7, 1988
Queen Elizabeth Hotel
Montreal, Quebec

6 et 7 avril 1988
Hôtel Reine Elizabeth
Montréal (Québec)

Environment Canada
Conservation and Protection

Environnement Canada
Conservation et Protection

Gouvernement du Québec
Ministère de l'Environnement
3900, rue Marly
Ste-Foy (Québec)
G1X 4E4

Association pour la prévention de la
contamination atmosphérique (APCA)
7127, rue de Lorimier
Montréal (Québec)
H2E 2N7

Commission de la santé et de la sécurité
du travail (CSST)
1199, rue de Bleury, 11e étage
C.P. 6056, Succursale A
Montréal (Québec)
H3C 4E1

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Cat. No. En 40-11/4-1988
ISBN 0-662-55778-6

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N° de cat. En 40-11/4-1988
ISBN 0-662-55778-6

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André Champoux
Technology Development and Technical Services Branch /
Direction du développement technologique et des services techniques
Environment Canada / Environnement Canada
Ottawa, Ontario
K1A 0H3
(819) 953-1199

The steering Committee of the Third Conference on Toxic Substances wishes to record it's appreciation of the efforts of the panelists for preparing the outlines of their papers and their subsequent delivery and to the panel moderators for guiding panelists and audience during the conference sessions.

Le Comité d'organisation du 3ième Colloque sur les substances toxiques aimerait noter son appréciation auprès des conférenciers pour la préparation de leur présentation ainsi qu'aux modérateurs pour leur aide soutenue lors du déroulement de la conférence.

Breda Nadon
Alain Bernier
Jules Brodeur
Michel Goulet
Pierre Robert
John Barter
André Champoux

Lucie Boisjoly
Marc Baril
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Michel Gauthier
Liette Roy
Guy O'Bomsawin

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INTERNATIONAL PERSPECTIVES FOR THE CONTROL OF TOXIC SUBSTANCES

DR. J. E. BRYDON

Head, Chemicals Division, Environment Directorate*
Organisation for Economic Co-operation and Development
Paris

International concern for the adequate control of toxic substances is generated:

1) by the known and unknown adverse effects of low amounts of toxic substances on human health and the environment;
2) by transboundary movement of toxic substances throughout the environment; and
3) by transboundary trade in bulk chemicals and articles containing them.

Many international bodies have chemical safety programs that address the various parts of the broad problem of toxic substances of concern to their particular clientelle.

INFORMATION ON AND INTELLIGENCE ABOUT TOXIC SUBSTANCES

Obtaining sufficient information on and intelligence about a toxic substance in relation to its commercial or environmental life cycle is the basis for any meaningful approach to the control of toxic substances.

New Chemicals

Depending upon the definition of a chemical, about 1,000 chemicals are annually introduced into commercial use world-wide. OECD countries decided several years ago to place special emphasis on new chemicals and developed policies for dealing with their potential hazards. They agreed that a base-set of data should be developed to permit an initial evaluation of the potential hazard of a chemical before it is placed on the market. Most OECD countries now have a notification or registration system to deal with new chemicals, incorporating the concept of the base set of data. One consequence is that industry does its own screening more effectively and that few hazardous chemicals are notified to the authorities. Furthermore, the concept of a base-set of data for an initial hazard assessment is being used beyond OECD countries.

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* The opinions expressed in this paper are those of the author and do not necessarily represent the views of the OECD or of the Governments of its Member countries.

Existing Chemicals

Of the millions of chemical substances known, about 100,000 are currently in commercial use. Various approaches are used by governments and international bodies to focus on a manageable number of existing chemicals in order to make decisions related to their potential hazards. The priority lists of chemicals to be investigated reflect various criteria and interests of those generating the lists. The OECD has developed a systematic approach for setting priorities which is based upon the use of commonly held selection criteria and which is now being applied in the OECD countries.

Gathering or generating information on chemicals on a priority list is a slow process, as is the evaluation or assessment of the hazard. The International Programme on Chemical Safety (IPCS) has a major program of international review of individual chemicals and has published almost a hundred Environmental Health Criteria Documents in a few years. The OECD countries have embarked on a program to speed up the process of testing, assessing and reviewing existing chemicals by co-operating in the systematic investigation of existing chemicals. The initial plans for this work were laid at a Workshop in Ottawa in November 1987. The first twelve chemicals of interest to several countries and agencies were selected. One country has taken the lead for each chemical and will oversee arrangements to share the work among the countries interested in each chemical. By avoiding duplication and by sharing the results, it is hoped and expected that the rate of augmenting the storehouse of information on priority chemicals will be increased.

Any Intelligence/Information program based on priority chemicals automatically leaves uncertainties about the tens of thousands of remaining existing chemicals. Programs for identifying qualitively and quantitatively the presence of chemicals in the environment and in our air or food exist on a sporadic basis. One of the few systematic approaches is the Japanese program of environmental monitoring, whereby many selected sites are monitored quantitatively for a few problem chemicals and fewer selected sites are monitored qualitatively for the presence of many chemicals. Such systematic approaches to monitoring need to be developed elsewhere. Co-ordination of such programs, both for the purpose of planning and effective use of the results, is needed at the international as well as at the national level. One important goal of such work is to establish the existing exposure situation of a chemical so that it can be considered in priority-setting exercises.

The OECD has initiated a project to address those chemicals which have a high potential exposure but which may not appear on priority lists. Of the 100,000 existing chemicals, 1,000 account for 99 percent of the total production volume. Production volume can be considered as an approximate indication of the exposure potential. The plan is, therefore, to develop an aggregated list of the 1,000 chemicals of highest production in OECD countries. Information about what data is available, what data is needed for which chemicals will be determined collectively. The project has two major goals. Everyone will have a better appreciation of the major chemicals having a potential environmental exposure, and a further criteria will be available for consideration in priority-setting activities.

Another international dimension of Information/Intelligence concerns the development of harmonized supporting instruments such as methodologies and guidelines. The OECD has produced about 75 Test Guidelines that are accepted in all OECD countries and now being used

increasingly world-wide. The OECD principles of Good Laboratory Practices have been extended world-wide through the IPCS. In addition to the wide application of such harmonized procedures, OECD countries have agreed to accept, for purposes of hazard assessments, data generated elsewhere using OECD Testing Guidelines and following OECD GLP Principles (Mutual Acceptance of Data). The IPCS and the International Agency for Research on Cancer (IARC), as well as OECD, have developed harmonized principles for hazard and risk assessment. OECD is currently preparing a Compendium of methodologies currently in use for exposure assessment, including those for the assessment of sources and of the environmental pathway and fate of a chemical.

MANAGEMENT AND CONTROL OF TOXIC SUBSTANCES

The Management and Control of hazardous chemical substances is a second phase of toxic substances programs after Information/Intelligence. It is convenient to address this aspect in two ways:

Direct risk reduction is designed to eliminate or limit the exposure to an individual toxic substance. All exposure routes to a target and all of the weak points in the entire cradle-to-grave commercial life cycle of a chemical are considered. Then, selective controls, standards and other management options are introduced to give the most efficient reduction of risk.

Internationally, the approach to direct risk reduction takes several forms and significant progress has been made in some areas. Standards for pesticides residues and other contaminants in food developed by IPCS are accepted universally as are work place air standards developed by ILO on a tripartite labor-management-government basis. It is more difficult to get international agreement on emission or effluent standards, or on air and water quality standards. It is extremely difficult to develop an agreed international approach to the total control of an individual toxic substance. In the OECD, concerted action has been undertaken on only one chemical - PCBs - via a Council Decision in 1973 that was upgraded in 1987 to ban all but existing electrical uses. Ten years of negotiation preceded a UNEP agreement in 1987 in Montreal for a partial control of CFCs. Asbestos and cadmium are two conspicuous examples where consultations and negotiations failed to reach agreement on an harmonized approach to control. There are several reasons for this situation. For nationalistic reasons, countries make their own decisions. Exposure situations may differ among countries. The socio-economic-political dimensions are usually different. Nevertheless, pressure for international action must be maintained because some chemicals, e.g. CFCs, pose a global environmental threat, and others, e.g. cadmium, which occurs in hundreds of articles, pose a problem as a result of international trade. The development of OECD and UNEP recommendations for notification of export of hazardous chemicals is one response to the need for some control of the trade of such chemicals.

Indirect risk reduction is achieved by integrating environmental protection principles and chemical containment measures into the operations of the various industrial and commercial sectors. By applying such good practices in, for example, the steel or textile industry, the

release of all chemicals to the environment will be decreased and the resulting exposure to any individual toxic chemical will be lowered. Inevitably, a major focus in all industrial sectors should be on waste streams and losses to air and to water, as well as the management of any resulting hazardous solid waste.

Internationally, a number of projects and activities have addressed the horizontal integration of environmental protection or good manufacturing practices into the various industrial sectors. The World Bank, the UNEP Industrial Programme, the OECD Environment Programme and the World Commission on Environment and Development, among others, have proposed specific policies to address the need for integration. The key issue now is the practical implementation of such policies. Specific attention is being given to waste streams and management of hazardous wastes by OECD, UNEP and the European Commission for Europe (ECE). OECD and UNEP are now about to address policies for developing and promoting low-waste technologies and reduction of waste at source, both of which should result in a decrease in the release of chemicals.

Broad implementation of these horizontal integration policies will result in a decrease in the release of all chemicals to the environment. They are the first line of defense against a specific toxic chemical which has multiple commercial uses. A key element in implementation is the selection of an effective indicator of the effectiveness of the application of the policies, for example, general emission controls. Such indicators are needed for purposes of self-regulation by industry or as a signal to government authorities that government intervention is needed, either to strengthen the general good industrial practices or to introduce stringent standards for the release of a specific toxic substance. Thus, indirect risk reduction achieved through horizontal integration policies should address the major risk of release of a specific toxic substance; direct risk reduction can be used for specific toxic substances, where the most benefit can be achieved.

THE PRIORITY SUBSTANCES PROGRAM OF THE CANADIAN ENVIRONMENTAL PROTECTION ACT

John A. Buccini, Ph.D.
Chief, Chemicals Evaluation Division
Commercial Chemicals Branch
Environment Canada

In my presentation this morning, I shall address the following three subjects:

1. Background of the existing chemicals issue.
2. Canada's strategy to deal with the issue.
3. Hi-lites of the CEPA Priority Substances program.

BACKGROUND

It has been more than twenty-five years since the publication of Rachel Carson's book Silent Spring. That book alerted the public to the unforeseen effects that could result from the use of chemicals in our modern society and argued that even those chemicals with the capacity to eliminate plague and pestilance could ultimately harm the ecosystem upon which all life depends. There developed a general awareness of this potential during the late 1960's and early 1970's resulting in the first wave of legislation in many countries to control toxic environmental contaminants. In Canada, the Environmental Contaminants Act was debated in Parliament in 1974 and 1975 and came into effect on April 1, 1976.

In recent years, chemicals seem to be in the news with increasing frequency, and almost always in a negative vein. Scarcely a week goes by without a story relating to leaking toxic dump sites, industrial accidents, the contamination of drinking water or food supplies, or other problems resulting from the global use of chemicals on an ever-increasing scale. In recent years there has occurred a number of disasters (Bhopal, India; Rhine River, Europe) that have underscored the fact that we have yet to master the use of the chemicals that we have, wittingly or otherwise, come to depend upon for our current standard of living.

Many nations are grappling with the complex problems, both short-term and long-term, posed by the use of these chemicals in modern society. There has developed a crisis of confidence in the abilities of governments and industries to manage chemicals effectively, to protect our citizens and to pass on a viable environment to future generations. As a result, environmental issues have come to occupy a unique position on the political agenda in industrialized countries. This is particularly the case in Canada where concern for the environment is directly linked to Canadians' perceptions of themselves and their country. For the first time in our history, concern for the quality of the environment has been either first or second (to jobs or the economy) in public opinion polls for the last two years or so. The federal government has been asked to respond to the concerns of the public ar to do so in a manner that is more effective than past efforts have been.

In the past, we have often assumed that nature would take care of the breakdown of chemicals into residues that would be harmless to humans and the environment. Inadequate evaluations were made of the potential damage that might be caused and, as a result, we have had to face up to a legacy of problems requiring remedial action. We now know that it will be many years before such persistent chemicals as polychlorinated biphenyls (PCB) will disappear from the Canadian environment or the environments of other countries around the world. The prospect of damage caused by chlorofluorocarbons (CFC) to the ozone layer that protects our planet from the effects of excessive ultraviolet radiation is another example of a problem caused by introducing a type of chemical into the world marketplace in the absence of an appreciation of the long-term effects on the global environment. In response to these problems the federal government has developed a strategy to cope with the existing chemicals issue.

THE STRATEGY

In developing a strategy for responding to the existing chemicals problem it was necessary to recognize the following factors:

1. There are more than 100,000 substances in global commerce.
2. Many chemicals will undergo transboundary movement once released to the environment, resulting in global or regional contamination.
3. The Canadian economy accounts for a few percent of the global trade in chemicals.
4. We have a large physical environment with a relatively small and unevenly distributed population.
5. The resources available within the federal government are limited and must be allocated wisely in dealing with the existing chemicals issue.

Considering both the domestic and global situations, the federal government has proposed a strategy that has two components, each dependent on the other to solve the existing chemicals problems in this country.

First, the Government of Canada has to improve its program to deal with the domestic problems associated with the proliferating use of chemicals in this country. I will discuss this in more detail in a moment, but I would like to mention the second component of the strategy before I do so.

Secondly, the Government of Canada acknowledges that international cooperative action is essential in assessing and controlling the environmental impacts of toxic chemicals. Canada has supported and will continue to press for international cooperative programs in order to ensure that appropriate and timely controls are developed for those toxic chemicals that are capable of contaminating the environment on a regional or global scale. Canada has been very active in the recent UNEP activities to control CFC use and in the OECD Chemicals Programme because we believe that all countries that participate in such multinational programs can make best use of the human resources available if we pool our efforts in testing, assessing and monitoring priority existing chemicals. When there is collective agreement to control a toxic chemical, then it is possible to avoid economic disruptions and pollution havens while moving to reduce releases of the chemical to the environment.

Thus the Canadian strategy involves a strengthening of our domestic programs coupled with a commitment to increasing international cooperative programs.

THE CEPA PRIORITY SUBSTANCES PROGRAM

By this time many of you will be familiar with the Canadian Environmental Protection Act (CEPA). This Act was originally tabled in Parliament in December 1986, for information, and following a period of extensive consultation was given first reading on June 26, 1987. It is expected that the Act will have Parliamentary approval by the Spring of 1988. The Act has, as its focus, a life-cycle management approach to toxic chemicals and will be administered to emphasize the complementary strategies of anticipation and prevention. We now accept as fundamental that after-the-fact remedies can no longer be an acceptable mode of doing business as the costs, in all senses, are too large. CEPA embodies an ecosystem vision of environmental protection encompassing air, land, water, all layers of the atmosphere and all organic and inorganic matter and living organisms. The Act recognizes environmental protection for its own sake while issuing a strong policy statement linking protection of the environment from the effects of toxic substances with the life and health of Canadians. Above all the Act improves the Federal Government's ability to control the release of toxic substances into the environment.

I am not going to review the whole act: instead I will focus on sections 12 and 13 that deal with "Priority Substances". CEPA requires the Ministers of the Environment and of National Health and Welfare to compile and publish a list of substances known as the Priority Substances List. This list will include substances that the Ministers are satisfied should be given priority in assessing whether they are toxic (as defined in section 11 of CEPA). This list will be the agenda for assessment and research activities that will be carried out by the two departments. The Act provides for nominations of substances to be made by individual citizens and obligates the Minister of the Environment to respond to each nomination. Additionally, the Ministers are empowered to consult with representatives of the various sectors of society (industry, public interest groups, provinces, labour) in developing the list.

The Minister of the Environment, The Honourable Tom McMillan, recently announced the creation of an advisory panel to develop this Priority Substances List. The membership of the panel is shown below:

PRIORITY SUBSTANCES ADVISORY PANEL MEMBERS

Don MacKay University of Toronto	Ann Robinson Ontario Ministry of Labour
Don Ecobichon McGill University	Bill Neff Canadian Chemical Producers Assoc.
Jack Siemiatycki Institut Armand Frappier	W. Charles Ferguson Director, Environmental Affairs, INCO
Daniel Green SVP, Montreal	Stuart Sullivan Energy and Chemical Workers Union

Carole Rubin
B.C. Committee for Alternatives to Pesticides

Ross Hall
McMaster University

The panel will be chaired by Dr. Ross Hume Hall, a professor of biochemistry at McMaster University, a former Chairman of Pollution Probe and a former member of the Canadian Environmental Advisory Council (a council that provides independent advice to the Minister of the Environment on his programs). The Advisory Panel will review and consider the criteria for selecting substances that should appear on the Priority Substances List. It is expected that priority substances will have one or more of the following characteristics:

1. The substance is poisonous.
2. The substance is persistent and thus likely to be dispersed over a wide geographic area.
3. The substance bioaccumulates in food chains.
4. The substance is in Canadian commerce and could enter the Canadian environment in significant amounts.
5. The substance has been detected in the Canadian environment.

The panel will be examining both the national and international body of scientific knowledge and is expected to provide a list of up to fifty substances to the Ministers by the middle of 1988. Following receipt of the advice of the panel, the Ministers will publish in the Canada Gazette the names of the substances that will be subjected to health and environmental hazard assessments.

Once a hazard assessment has been completed, CEPA requires that the assessment report be published. All decisions to control or not to control a chemical are open to appeal to a Board of Review by any member of the public.

In carrying out the hazard assessment of a priority substance, the following data elements will be reviewed.

1. Chemical Identity and Physical and Chemical Properties: Knowledge of these factors is necessary to understand the behaviour of any compound with respect to its exposure pattern as well as its toxicological characteristics. Since the use of a chemical is largely dependent upon its physical and chemical properties, these data are usually readily available or easily retrieved.
2. Exposure Data: Included are those data relevant for assessing exposure via the workplace, consumer products or the environment. In addition, information about the chemical's transport, distribution, and transformation in the environment is of great interest in determining exposure patterns.
   Exposure information could be derived from data on actual production, use pattern and disposal. Use patterns indicate the approximate amount of a chemical in use and the likely pathway into the environment. Other characteristics of the exposure pattern include the frequency, intensity and duration of releases and populations exposed.
   Often it is not possible to make a quantitative assessment of human or environmental exposure due to lack of data. Moreover, many

chemicals are handled in a great variety of ways including unknown end-uses. However, a qualitative judgement of type and relative degree of exposure can often be inferred indirectly from certain basic physical and chemical data and from a description of the function and intended use of a chemical.

3. Effects on Experimental Animals and In-Vitro Test Systems: The data relevant to the metabolism in and effects on animals and in-vitro systems are used to model human health conditions. Information of particular interest for assessing health effects includes toxicity, the species affected, the route(s) of exposure for which the most important toxic effects occur, the frequency and duration of exposure, dose-response relationships, etc. Internationally, there is broad agreement on many current test procedures and, to a certain extent, on interpreting test data.
4. Effects on Man: Data from case observations, clinical trials, and epidemiological studies, together with interpretation of data concerning effects on experimental animals and in-vitro test systems, form the basis for human health effects determinations.
5. Effects on the Environment: Included are those data relevant to understanding the impact on some populations within the ecosystem and the bioaccumulation potential. Environmental effects may be divided into two general categories:

   (i) bioaccumulation potential as an indicator of a chemical's ability to concentrate in living organisms; and
   (ii) toxic effects, as a measure of the potential impact of a chemical on the structure and function of some populations within the ecosystem.

   Predicting effects on the ecosystem from laboratory tests presents significantly different problems compared with those encountered in predicting health effects. For health effects, individual toxic end-points are relatively well-defined and understood. There is far less consensus on the significance of ecotoxicological test results. For this reason, estimates of ecological effects involve greater uncertainties, which must be taken into account in the review process.

If the review of a priority substance leads to the conclusion that the substance is toxic (as defined in section 11 of CEPA) then the substance can be added to the Schedule to the Act and regulations may be created to control almost any aspect of the life-cycle of the substance. This coupled with a strong enforcement program should serve to reduce the risks associated with the use of the substance.

Somewhat simplified, risk refers to the probability of harm occurring as a result of a given level of exposure to a known hazard even when data are available for all the evaluation criteria that I have described we are still left with some scientific uncertainty. Decisions on scheduling a toxic substance under the Canadian Environmental Protection Act will be based on the best scientific information available. While science will address concerns about the safety of chemicals it will never dispel them. In a world of incomplete information, decisions by regulatory agencies will inevitably

involve judgements about the acceptability of risks. These value judgements must take into account social and political considerations as well as scientific information. The value judgements must be made only after all parties have had an opportunity to input to the regulatory decision-making process.

Well, this has been a rather quick review of the legislative requirements and scientific considerations that will be involved in implementing the CEPA Priority Substances Program. As I mentioned earlier, the public has asked for the Federal Government to improve its program for assessing and controlling toxic substances. With the CEPA provisions and the additional resources that have recently been allocated to the program, I believe that we are in a position to start to cope with the problem. However, we are faced with a very large task and the problems will not be solved overnight. With an estimated 35,000 substances in use in Canada (in countless combinations), priorities must be set if we are to apply our staff resources in the most productive fashion. We are also strongly committed to pursuing international cooperative programs with provincial governments and other countries on these substances to avoid duplication of work carried out in other jurisdictions and to accelerate the rate at which hazard assessments may be completed. With the enthusiasm and the sense of commitment that I have recently observed in my counterparts in other countries, I feel that real progress will be made in the coming years.

INITIATIVES IN ONTARIO FOR THE MANAGEMENT OF TOXIC SUBSTANCES

By

Dr. David Balsillie
Ontario Ministry of Environment

Paper unavailable at time of printing

The Federal Strategy for Air Toxics Control in the United States

Jeanette Wiltse
U.S. Environmental Protection Agency

ABSTRACT

The major objectives of the current strategy for air toxics control in the United States are Federal regulation of nationwide sources such as municipal waste incinerators and hazardous waste treatment and storage facilities, and State, and local assessment and control of important local sources that are not nationwide in impact. Recent judicial interpretation of section 112 of the Clean Air Act, the major authority for air toxics control, and reexamination of section 112 by the U.S. Congress may lead to a major restructuring of this regulatory authority.

Introduction

The topic of this discussion is the Federal Strategy for Air Toxics in Control in the U.S. I shall describe for you the current air toxics program at the Environmental Protection Agency.

However, before I do I want to expressly recognize that the past year has been one of national debate in the U.S. concerning almost every aspect of air pollution including air toxics. I have made a list of these major air pollution issues.

Table 1
MAJOR AIR POLLUTION ISSUES

Criteria pollutants (e.g. O_3, NOx, SOx)
Indoor air
Stratospheric ozone
Acid rain
Air toxics

The current debate in the U.S. about these issues will continue in the year ahead and may result in significant change in national policy and legislation. There are several reason for the fact that all of these are coming to a head at one time. One is that Clean Air Act deadlines for attainment of air quality criteria for ozone have been missed by many areas of the country. The question of how to bring these areas to attainment is one center of debate. Another reason is that a knowledge base has accumulated in this decade on problems such as indoor air quality (including radon in buildings), acid rain, and air toxics, as well as stratospheric ozone. This growing knowledge has defined and raised our level of concern about these problems and made them national issues. The third reason is that our Clean Air Act is overdue for reexamination and

enough to portend action to amend the Clean Air Act, and already a number of bills have been introduced in the Congress to do just that, including one on air toxics which I will describe after I outline our current air toxics program.

Other factors in this policy ferment are the Federal elections this year and the fact that we will have a new administration in 1989. With all of this going on I can tell you some of the history and current events in air toxics, but only speculate about what the future may bring.

Current Program

The basis for our air toxics strategy is a study done about four years ago. The purpose was to get a better picture of what the dimensions of the air toxics problem are in the U.S. I won't try to give you all the details of the study. In general, the approach was to take what we knew about carcinogenicity of chemicals and about their release and, where known, their levels in the air, and make the best estimates we could of health risks. We used quantitative dose response extrapolation models to estimate cancer risk to exposed populations. From this we estimated how much increased cancer incidence per year could be expected from various kinds of sources and emissions such as water treatment works, mobile sources, and manufacturing sites. The methodological limitations of such estimations are obvious to those familiar with assessment of toxicant risk. Also, the study did not attempt to assess systemic toxicity, only carcinogenicity. Nevertheless, it gave us a start. The results led us to conclude that our greatest attention should be given to the sources listed in Table 2. In addition we concluded from the study that past control of volatile organic compounds to prevent ozone formation has reduced risk from organic carcinogens substantially.

Table 2

PRIORITY ROUTINE-RELEASE SOURCES OF RISK

Major Pollutants

Metals: chromium, cadmium
Products of Incomplete Combustion: organic particulates
Organics: benzene, chloroform, carbon tetrachloride, formaldehyde

Major Sources

Widespread small sources: motor vehicles, home heating (woodstoves),solvent users, gas stations.

Individual large sources: chemical plants; refineries; large combustion sources; waste treatment, storage and disposal facilities.

To effectively carry out projects to address these sources our strategy combines research and regulation at the Federal level with State and Local agency efforts. The Federal regulatory role is to address the sources that

are nationwide and to provide technical support to State and local agencies to address sources and problems that are important in their geographic areas, but not uniform nationwide.

Our current Federal actions are summarized in Table 3. As you see in Table 3, we are addressing particulates and combustion products from both point sources and mobile sources, as well as from woodstoves. Control of emissions of individual chemicals are the objectives of National Emission Standards for Hazardous Air Pollutants.

In addition to directly regulating existing and new sources of hazardous air pollutants, we continue to try to improve on the toxicant control that result from state implementation plans and mobile source controls programs to meet air quality criteria for particulates and ozone.

Table 3

CURRENT PROGRAM - CLEAN AIR ACT (CAA)

- o State Implementation Plans for meeting Particulate matter (PM10) and Ozone criteria
- o New Sources Performance Standards
  - Wood Stoves
  - Municipal Waste Combustors (MWC)
  - Synthetic Organic Chemical Manufacturing Industry
- o National Emission Standards for Hazardous Air Pollutants (112 CAA)
  - Under development for about 23 source categories
- o Prevention of Significant Deterioration
  - Unregulated Pollutants
  - MWC Guidance
- o Mobile Sources
  - Diesel Particulates
  - Onboard Controls
  - Catalyst Program
  - Methanol Regs
  - Fuel Additives and Composition Regs
  - Anti-Tampering and Misfueling

As you can see from Table 4 we have broadened the number of statutes used to address air toxics include just about all the authorities we administer. Moreover under these authorities we are addressing many sources identified in our original study.

Table 4

CURRENT PROGRAM - OTHER AUTHORITIES

- o Resource Conservation and Recovery Act (waste control)
  - Treatment, Storage, and Disposal Facilities
  - Used oil Restrictions
  - Hazardous Waste Incineration
- o Fungicide, Insecticide and Rodenticide Act
  - Carbon Tet, Other Inerts

- Ban on Use; Application Restrictions

o Superfund
  - Site Cleanups
  - Mandatory Community Emergency Preparedness Under Title III

o Clean Water Act
  -Sludge Incineration Regulation

Table 5 is a list of source of individual organic compound emissions that are being considered for regulation. These sources were identified by considering the potential risk posed by many sources of the individual chemicals named in the table. From these numerous sources the listed sources were selected because they potential cause significant risks and they are nationwide sources suitable for Federal control.

Table 5

SOURCE CATEGORIES BEING CONSIDERED FOR NESHAP REGULATION

Industrial cooling towers (chromium)
Electroplating (chromium)
Commercial sterilizers (ethylene oxide)
Dry cleaning (perchloroethylene)
Decreasing (perc, trichloroethylene, methylene chloride)
Coke oven by-product plants (benzene)
Demolition and renovation revision (asbestos)
Hazardous organic NESHAP for 13 process source categories (covers 8 organic compounds)

The state and local programs we are encouraging and supporting with grant funds and technical support are summarized below.

Table 6
STATE/LOCAL PROGRAM
FOUR MAJOR THEMES

1. Accept NESHAP Enforcement Delegation
   -- More Sources
   -- More Complex Sources
2. Address High Risk Point Sources
   -- High Individual Risks
   -- Potentially Many Sources
3. Address High Risk Urban Problems
   -- High Individual Risks in Urban Areas
   -- Caused by Multi-Pollutant/Multi-Sources Interaction
4. Enhance State/Local Capability
   -- Develop Their Own Programs
   -- Carry out the Above Themes

In general we are encouraged by the number of new air toxics programs being established at the State and local level. These program building efforts are limited in many cases by the funds we and the State can provide. It should be noted that several states have programs that are already very extensive and sophisticated.

As ways to give necessary technical support to State and local program

we have established a program of national workshops to bring together staff of EPA, State and local agencies to work on subjects such as dispersion modeling, incinerator emissions, and how to build air toxics programs. Also we have established a National Air Toxics Information Clearinghouse, the heart of which is a very large interactive computer data base. Last year we started operating a Control Technology Center (CTC) which provides direct technical engineering assistance to State and local agencies. The Advisory Board for the CTC is composed of EPA and state and local representatives. We are currently considering establishment of a Health Risk Information Center along the operating lines of the CTC.

Now to the forces at work to change some of our past approaches.--

Last summer a decision came down from the United States Court of Appeals for the District of Columbia. The case was one in which the the National Resources Defense Fund challenged the way EPA has implemented section 112 of the Clean Air Act -- National Emission Standards for Hazardous Air Pollutants. The Court said that we had impermissibly considered costs and feasibility of emissions controls in setting standards. The Court gave us a new way to set these standards. It prescribed a two step decision in which we first must decide, on the basis of health considerations alone, what an acceptable/safe level of exposure is from a source; this becomes the set point for the maximum allowable emissions from the source. Then we can use cost and feasibility to add an ample margin of safety to lower the allowance emissions. This case particularly concerned our emissions standards for vinyl chloride, but similar challenges were pending for other standards. The result is that we have court orders to reconsider the standards for several categories of sources of radionuclides and benzene emissions. These particular reconsiderations are the immediate result of the decision. However, we may face the same reconsideration of several other standards as litigants continue to challenge past decisions. One result of course is that we are delayed in carrying out new actions under section 112 while we devote resources to reconsidering previous actions. Another result is Congressional attention to the effect of this decision on our activities and perhaps further impetus to legislative changes. The existing standards remain in effect, pending these reconsideration.

A change we might see from the Congress if a current draft Senate bill were enacted would be an entirely restructured section 112. Concerns by the Senate committee that drafted the bill included the small number of standards we have established under 112 and a desire for much more Federal as opposed to State regulation. The bill would require that the best control technology be used for major sources of a list of more than 200 chemicals. Beyond this, under some circumstances additional control would be required if residual risks were significant after initial controls were installed. The bill additionally would establish a programs for reduction of emissions of area sources e.g. mobile sources pesticide application, and for sudden, emergency release with potentially acute exposures.

In summary, we are carrying out our current programs, reexamining certain of our standards and keeping an eye out for a potentially fundamental legislative restructuring of our Act.

GASEOUS TOXICS: MONITORING IN A LARGE METROPOLITAN AREA – THE SAN FRANCISCO BAY AREA EXPERIENCE

By

Mr. Dario Levaggi
Bay Area Air Quality Management District, United States

Paper unavailable at time of printing

EXPOSURE AND RISK OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH): BENZO(a)PYRENE AS CASE STUDY

By

Dr. Paul Lioy
Robert Wood Johnson Medical School, New Jersey, USA

Paper unavailable at time of printing

MEASUREMENT of POLYCYCLIC AROMATIC HYDROCARBONS (PAH) in the AMBIENT AIR (TORONTO, ONTARIO and MONTREAL, QUEBEC)

T. Dann
Pollution Measurement Division, Environment Canada

INTRODUCTION

The category of compounds known as polycyclic aromatic hydrocarbons (PAH) have received a great deal of attention in recent years because some species of PAH are known human carcinogens.[1,2] Because PAH result from the incomplete combustion of fossil fuels they are ubiquitous in the atmosphere. Although natural sources of PAH do exist, anthropogenic sources are the major contributor and urban and near industrial ambient air concentrations of PAH have been shown to be two to three orders of magnitude greater than remote or rural concentrations.[3]

A great deal of urban ambient air measurement data for PAH has been reported in the literature dating back to the early 1960's.[3,4] Although a variety of sampling and analytical approaches have been used, making data comparability a problem, there is evidence that urban concentrations of PAH declined during the 1970's with the advent of legislated particulate controls and with the reduction in use of coal as a residential/commercial heating fuel.[3,4] However, even at current measured ambient levels, there is concern that PAH's pose a risk to human health. The increasing use of wood as a residential fuel, rapidly increasing heavy duty diesel truck fleets and greater reliance on incinerators for the disposal of municipal refuse may lead to a reversal of the decline in ambient PAH and possibly to future increases.

In order to establish a data base on current levels of PAH in Canadian urban areas, the Pollution Measurement Division and Analytical Services Division, Conservation & Protection, Environment Canada established a monitoring program for PAH at sites in Toronto, Ontario and Montreal, Quebec. Particulate and gaseous PAH compounds were collected using a high-volume sampler equipped with Teflon-coated glass fibre filters and a polyurethane foam (PUF) backup trap. Analyses were conducted by gas chromatography mass-spectrometry, (GC-MS). Results are reported for the filter retained fraction of PAH (particulate fraction) and the polyurethane foam retained fraction (gaseous fraction). Twenty-four hour samples were collected on a six-day schedule at the Toronto site for the period August 1984 to July 1986 and at the Montreal site for the period October 1984 to May 1986. The sampling and analytical methods employed were refinements of earlier methods employed in studies of PAH concentration in the ambient air in Whitehorse, Yukon Territory,[5] Sydney, Nova Scotia[6] and Kitimat, British Columbia[7] during the years 1981 to 1984.

This report will provide a summary of the PAH data collected at the Toronto and Montreal sites. The results will be discussed in terms of the sampling methodology employed and in terms of environmental significance. Potential emission sources of the measured PAH compounds will be identified based on available emission inventory data and from relationships between compounds in the ambient data set. Measurements from Toronto and Montreal will be compared to recently reported results from other North American urban areas and from urban areas in other parts of the world.

BACKGROUND

Structure and Nomenclature

Polycyclic organic matter (POM) is a generic term for a large and diverse class of compounds which contain two or more fused aromatic (benzene) rings. These rings may be comprised totally of carbon atoms or may contain rings with atoms of nitrogen, oxygen, sulphur or other compounds substituted for one or more of the carbon atoms. POM is generally subdivided into two categories on the basis of the atomic constituents of the rings. These categories are polycyclic aromatic hydrocarbons (PAH) and heterocyclic polynuclear aromatic hydrocarbons (HAH).

PAH contain only carbon atoms in the aromatic rings. The PAH category is usually further subdivided into compounds with two or more fused benzene rings and those that contain a cyclopenta ring in addition to one or more benzene rings. The latter are referred to as non-alternate polycyclics. When substituents are attached to the rings, the number and diversity of PAH compounds is increased dramatically. These substituents can include the nitro (NO_2), methyl (CH_3), amino (NH_3) and ketone (carbonyl) functional groups. Within the PAH class, minor changes in structure and changes in location of substituents can greatly affect oncogenic properties.[1]

Heterocyclic polynuclear aromatic hydrocarbons include heterocyclic nitrogen compounds also called aza-arenes, heterocyclic oxygen compounds (oxa-arenes) and heterocyclic sulphur compounds (thia-arenes). A variety of substituent groups can also be attached to heterocyclic rings. The heterocyclic polynuclear aromatic hydrocarbons as a class have been studied much less than the PAH and although increasing attention is being focused on them, published information on physical properties, analytical techniques and ambient concentrations is relatively scarce.

Available Sampling and Analytical Techniques

PAH compounds of interest span a wide range of molecular weights and their physical properties vary accordingly. Vapor pressure is a particularly important property in relation to sampling techniques, as compounds with low vapor pressures are usually associated with particulate matter and compounds with higher vapor pressures are found as vapors. Experiments have shown that two to four ring PAH exist predominantly in the vapor phase while higher molecular weight PAH can exist either as vapor, adsorbed to particulate matter, or both, depending on temperature.[8,9]

Historically, most sampling efforts for atmospheric PAH have been limited to the collection of particulates on filters using a high-volume sampler. In more recent years, this type of sampling approach has been modified by the addition of an adsorbent trap following the filter in order to collect vapor phase PAH. The most commonly employed adsorbent has been polyurethane foam (PUF) because of its ease of handling and good collection efficiency for most PAH compounds of interest. Some researchers have employed granular sorbents such as XAD or Tenax.[10]

It has been well documented that losses of PAH from filter surfaces can occur due to desorption of PAH from particulates in the filter surface (sometimes referred to as blowoff) or due to chemical re-arrangement of the PAH due to interaction with oxidizing or acidic species in the air such as ozone, nitrogen dioxide, nitric acid and sulphuric acid.[11,12,13,14] Even sampling schemes employing a backup gaseous collection system may not accurately represent the phase distribution of PAH in the ambient air.[15] However, until further improvements in sampling technology occur,

the high volume filtration sampler with backup sorbent collection system is considered to be the sampling method of choice.[10]

Analytical techniques for PAH have evolved considerably from simple fluorescent techniques to computerized gas chromatography/mass spectrometry. The main advances in analysis have been in relation to improved resolution and an increase in the number of positively identified compounds.

FIELD MEASUREMENT PROGRAM

Approach

Sampling was carried out using a modified high-volume sampler equipped with a backup polyurethane foam sorbent trap. Analysis was carried out by gas chromatography with mass selective detection. Twenty-eight different PAH compounds, (25 resolved peaks) including four methyl substituted PAH, were identified and quantified in each sample. These compounds were chosen because (a) standards were readily available, (b) they were commonly reported to be present in urban air from other monitoring programs and (c) the sampling and analytical methodology employed was adequate for their quantification.

Sampling Site Locations

Samples were collected at two sites (1) Perth Avenue (Junction Triangle), Toronto, Ontario and (2) Boulevard St. Jean Baptiste (Pointe-aux-Trembles), Montreal, Quebec. The Toronto site is an Ontario Ministry of the Environment monitoring site (Ontario site #31120); the Montreal site is a National Air Pollution Surveillance (NAPS) monitoring location (NAPS station #50103). Both sites were also being used in conjunction with a volatile organics sampling project.

The Toronto site was located northwest of the downtown core in a 0.7 km^2 area referred to as the Junction Triangle. The sampler was located on the roof of a school 11 m above ground; the nearest major street was approximately 30 m to the east and had an average daily traffic volume of less than 10,000 vehicles per day. There are approximately 6,000 people living in the Junction Triangle area. Twenty small industries are also located in the Junction and the area is bounded by major railway lines on all sides. This area of Toronto has had a long history of residents voicing concerns over possible health impacts of the nearby industries.

The Montreal site was located near the north-east tip of Montreal Island. The monitoring shelter was situated in a public park in the centre of a residential area. The closest road was approximately 10 m north of the site and had an average daily traffic volume of 13,000 vehicles. The sampler was situated 4 m above ground level. A number of petroleum refineries were located to the west and southwest of the monitoring site.

Experimental

Sampling. A custom modified hi-volume sampler was used for the collection of samples as shown in Figure 1. Hi-volume sampler modifications included the addition of a dry gas meter, the addition of a sorbent canister and the movement of the blower motor to a position outside the shelter. The blower exhaust was ducted approximately 3 m away from the sampler intake.

Teflon-coated glass fibre filters (Pallflex Emfab TX40H120WW) of dimensions 20 cm x 25 cm were used as received from the manufacturer. From sheets of open-cell type polyurethane foam (PUF) with a density of 22.4 kg/m^3, two 7.5 cm x 7.5 cm diameter plugs were cut for insertion in the glass liner of the backup sorbent trap.

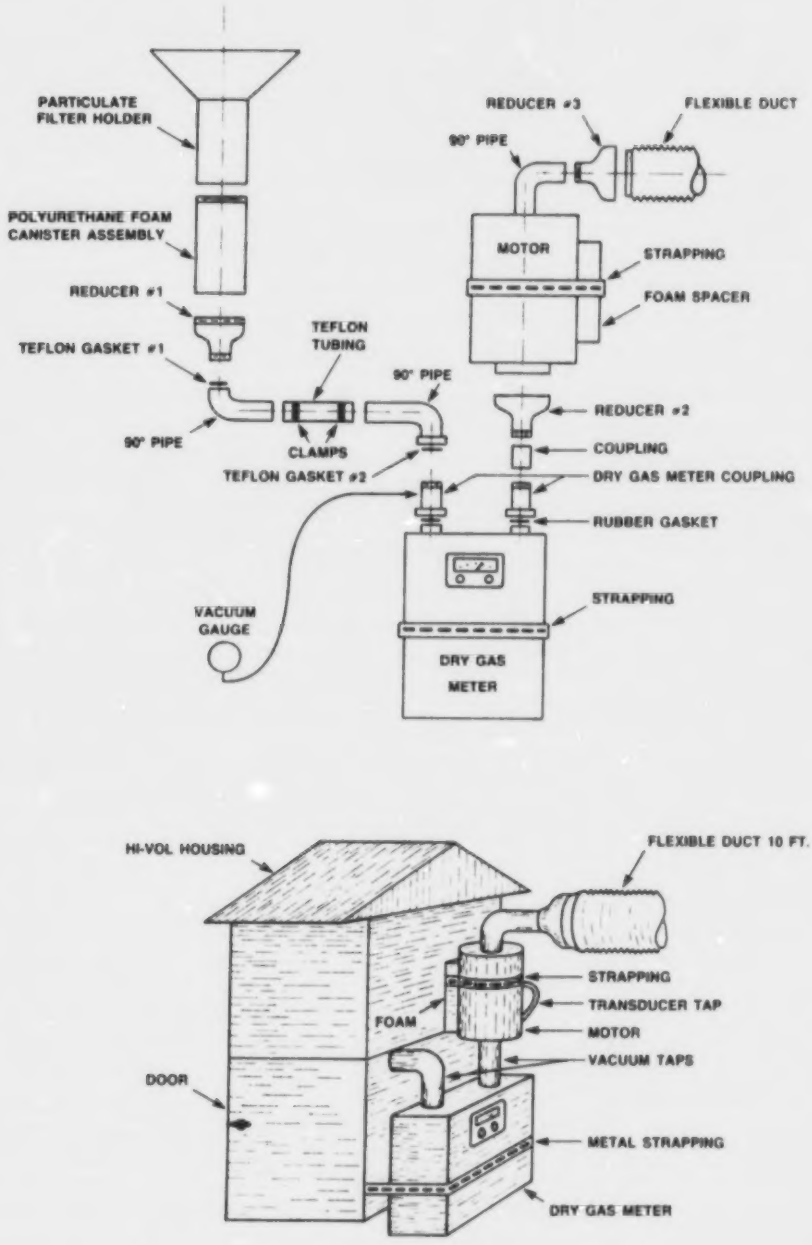

Figure 1: Modified Hi-Vol Sampling System for PAH

PUF plugs were cleaned before use by extracting for 24 hours with methanol followed by cylohexane in a Soxhlet apparatus. After extraction, the plugs were air dried for about 16 h.

The samplers operated at flow rates of 600 to 700 L/min. Samples were collected over 24 hours (midnight to midnight) and total sample volumes ranged from 850 to 1050 m^3.

Sample Recovery. Each filter was spiked with 2.5 µg each of 4 isotopically-labelled PAH standards (d_{10}-anthracene, d_{10}-pyrene, d_{12}-benzo(a)anthracene and d_{12}-perylene) and placed inside a pre-extracted soxhlet apparatus. The sample was extracted with 250 mL of benzene for 16-24 h at a rate of 5 to 8 cycles/h. The raw extract was then filtered through Na_2SO_4 and concentrated to ~5 mL by roto-evaporation. Approximately 10 mL of cyclohexane was added and the sample was roto-evaporated down to ~1 mL. This was repeated once to ensure complete replacement of benzene by cyclohexane.

Foam plugs were treated in the same manner as the filters, except that cyclohexane was used in the soxhlet extraction and the raw extract was roto-evaporated down to ~1 mL.

Sample Cleanup. A silica gel column, 20 cm x 1 cm ID containing 25 g of activated silica gel and 1 g of Na_2SO_4 was pre-washed with 50 mL of hexane. When the hexane had drained to bed level, the raw extract was quantitatively transferred onto the column. The column was eluted with another 50 mL of hexane and this hexane fraction was discarded. The PAHs in the sample were then eluted with 150 mL of benzene. This benzene fraction was concentrated to 1-2 mL by roto-evaporation, transferred to a graduated test tube, and further concentrated by UHP nitrogen blow-down at ambient temperature in a fume hood. The final purified extract volume was typically 0.5 mL.

Analysis. A 1 µL aliquot of the final purified extract was analyzed using an HP 5890 gas chromatograph interfaced directly to an HP5970 mass selective detector (MSD). The operating conditions for analysis are given in Table 1. Calibration was performed using a standard mixture of 28 PAH compounds at concentrations of 1-5 ng/mL. Quantification of individual PAH compounds was by means of comparison with the external calibration standard. Although 28 compounds were present in the standard, some were unresolved under the analytical conditions used so only 25 individual results were reported for each sample.

Quality Assurance. The temperature compensated dry gas meters used in the samplers were calibrated in the laboratory using a Roots rotary vane meter referenced to the Dominion Bureau of Standards. Temperature and pressure corrections (to 1 atmosphere and 25°C) were applied to recorded total gas meter volumes.

Collection efficiencies were typically poor for acenapthylene and acenapthene; the collection efficiencies for fluorene and 2-methyl-fluorene were poor at temperatures over 10 °C. Collection efficiencies for other compounds were calculated to range from 95% to >99% over the temperature range experienced in the field.[16] Losses of PAH from filter samples can also occur due to chemical re-arrangement and interactions with ambient nitrogen dioxide, nitric acid, ozone and sulphur dioxide.

The calibration standard containing 28 PAH compounds was prepared from stock solutions every one to two months and was checked against commercially

GC	
Column	30 m DB5 Fused Silica, 0.25 mm ID and 0.25 µm film thickness
Injector	On Column, 1 µL injection
Carrier	Helium, approximately 0.5 cc/min
Initital Temperature	90°C
Final Temperature	280°C
Temperature Rise	90°C for 1 min, 15°C/min to 200°C, 5°C/min to 280°C, 280°C for 10 min.
MSD	
Internal Temperature	290°C
Source Temperature	200°C
Ionization	Electron Impact
Electron Energy	70 eV
Analysis Mode	Selective Ion Monitoring (SIM), 5 step program with minimum of 2 ions per compound, 25 msec dwell per ion

TABLE 1 - GENERAL OPERATING PARAMETERS for HP GC/MSD ANALYSIS of PAH SAMPLES

available PAH mixtures. The calibration standard was run before and after each sample batch. An NBS standard reference material (SRM 1649) containing certified values for 5 PAH was also analyzed periodically.

At the start of the program, one filter and foam sample per batch were spiked with isotopically-labelled surrogate standards. Approximately six months into the program, spiking began on every filter and foam sample and the percentage recoveries were calculated and reported for each sample. The surrogates represented compounds containing between 3-5 aromatic rings: d_{10}-anthracene, d_{10}-pyrene, d_{12}-benzo(a)anthracene and d_{12}-perylene. The mean of the surrogate recoveries in Montreal and Toronto ranged from 75 to 85%. Concentrations were not corrected for surrogate recovery, however, results were not used if recoveries were less than 60%. The spiking program served to indicate the effectiveness of sample preparation and cleanup and of analytical procedures.

Analytical detection limits were 50 ng per PAH compound per sample. For a 900 m^3 sample volume this resulted in an ambient air detection limit of 0.06 ng/m^3 for each PAH compound.

RESULTS

A total of forty-two 24-hour samples were collected at the Toronto site during the period August 22, 1984 to July 12, 1986. Samples were usually taken once every six days but only every second sample was submitted for analysis. Of the forty-two samples analyzed, eight were collected in the winter months (December, January and February), fourteen in spring, eight in summer and twelve in fall. For all samples, results were available separately for filters and PUF plugs, for most samples, front and back PUF plugs were analyzed separately.

For the purposes of this report, particulate PAH is defined as the fraction captured on the filter and vapor PAH as the fraction captured on the two foam plugs. It should be noted that the sampler filter/foam PAH distribution may not accurately represent the actual particulate/vapor phase distribution in the ambient air. PAH compounds adsorbed to particulate matter may be "stripped off" or volatilized during sampling or alternately vapor phase compounds may be trapped on the particulate matter adhering to the filter.

In Table 2, the mean, standard deviation, median, maximum and minimum of the 24 h vapor plus particulate PAH concentrations at the Toronto site are given. Concentrations below detection limit were assigned a value of 0.0 ng/m^3 for calculation and reporting purposes. For each PAH compound, the mean fraction found as vapor and particulate over the study period is shown in Figure 2. From Figure 2, it can be seen that three ring PAH were found predominantly as vapors and five or six ring PAH predominantly as particulate. Most four ring compounds had a substantial vapor fraction.

The collection efficiency of PUF for acenapthylene, acenepthane and fluorene was generally poor and measured values are lower than those actually present in the ambient air. The PAH compounds with the highest mean concentrations at the Toronto site were phenanthrene at 25.6 ng/m^3, fluoranthene at 4.9 ng/m^3 and pyrene at 3.9 ng/m^3. These three compounds were collected primarily as vapors. Filter retained PAH compounds (particulates) found in the highest concentrations were benzo(b,k)fluoranthene at 1.3 ng/m^3, benzo(e)pyrene at 0.5 ng/m^3 and benzo(g,h,i)perylene at 0.8 ng/m^3. The mean concentration of benzo(a)pyrene at the Toronto site was 0.3 ng/m^3 with a maximum concentration of 3.1 ng/m^3.

In Montreal, a total of twenty-nine 24 h samples were collected during the period October 27, 1984 to May 20, 1986. As in Toronto, samples were usually collected once every six days and every second sample set was submitted for analysis. Because of sampler operational problems, samples were collected predominantly during the winter (10 samples) and spring seasons (11 samples). Only three samples were collected during the summer months and five during fall. Table 3 presents a summary of mean particulate plus vapor concentrations of PAH compounds at the Montreal site. The standard deviation of the daily mean concentration and the median, maximum and minimum daily concentrations are also included. In Figure 3, the mean fraction of each compound collected as vapor or particulate is shown.

PAH compounds found with the highest mean concentrations were phenanthrene at 12.7 ng/m^3, fluoranthrene at 6.2 ng/m^3 and pyrene at 5.1 ng/m^3. Despite poor and variable collection efficiencies, measured concentrations of acenaphthylene and fluorene were also relatively high. Phenanthrene was collected predominantly as a vapor at the Montreal site, while pyrene and fluoranthene were essentially equally divided between vapor and particulate. Filter collected particulate compounds found with the highest mean concentration were benzo(b & k)fluoranthene at 3.3 ng/m^3, benzo(e)pyrene at 1.3 ng/m^3 and benzo(g,

COMPOUNDS	MEAN	STD. DEV.	MEDIAN	MAX.	MIN.
Acenaphthylene*	4.12	5.98	1.68	25.37	0.21
Acenaphthene*	2.24	2.04	1.66	12.22	0.00
Fluorene*	5.51	4.37	4.50	25.39	0.00
2-Methyl-Fluorene	3.66	2.34	3.14	11.72	0.45
Phenanthrene	15.64	8.68	14.47	34.64	2.90
Anthracene	1.60	2.85	0.94	14.14	0.00
Fluoranthene	4.91	2.70	4.82	13.18	1.01
Pyrene	3.87	2.88	3.36	14.63	0.63
Benzo(a)Fluorene	0.53	0.48	0.45	2.58	0.00
Benzo(b)Fluorene	0.27	0.27	0.23	1.53	0.00
1-Methyl-Pyrene	0.18	0.21	0.13	1.01	0.00
Benzo(g,h,i)Fluoranthene	0.49	0.69	0.32	3.43	0.00
Benzo(a)Anthracene	0.40	0.92	0.17	5.78	0.00
Chrysene & Triphenylene	0.73	0.58	0.54	3.38	0.18
7-Methyl-Benzo(a)Anthracene	0.00	0.00	0.00	0.00	0.00
Benzo(b & k)Fluoranthene	1.26	1.45	0.83	8.20	0.16
Benzo(e)Pyrene	0.48	0.60	0.30	3.43	0.00
Benzo(a)Pyrene	0.30	0.52	0.16	3.14	0.00
Perylene	0.04	0.11	0.00	0.61	0.00
2-Methyl-Cholanthrene	0.02	0.13	0.00	0.81	0.00
Indeno(1,2,3-cd)Pyrene	0.46	0.62	0.29	3.65	0.00
Dibenzo(a,c) & (a,h)Anthracene	0.04	0.09	0.00	0.51	0.00
Benzo(b)Chrysene	0.04	0.13	0.00	0.72	0.00
Benzo(g,h,i)Perylene	0.07	1.16	0.47	6.64	0.00
Anthanthrene	0.02	0.05	0.00	0.23	0.00
TOTAL PAH	**47.57**	**27.26**	**44.09**	**162.63**	**8.70**

* Collection efficiency poor and dependent on ambient temperature (see text)

TABLE 2: SUMMARY of VAPOR PLUS PARTICULATE PAH (ng/m^3) in TORONTO (October 1984 - July 1986 - 42 Sampling Days)

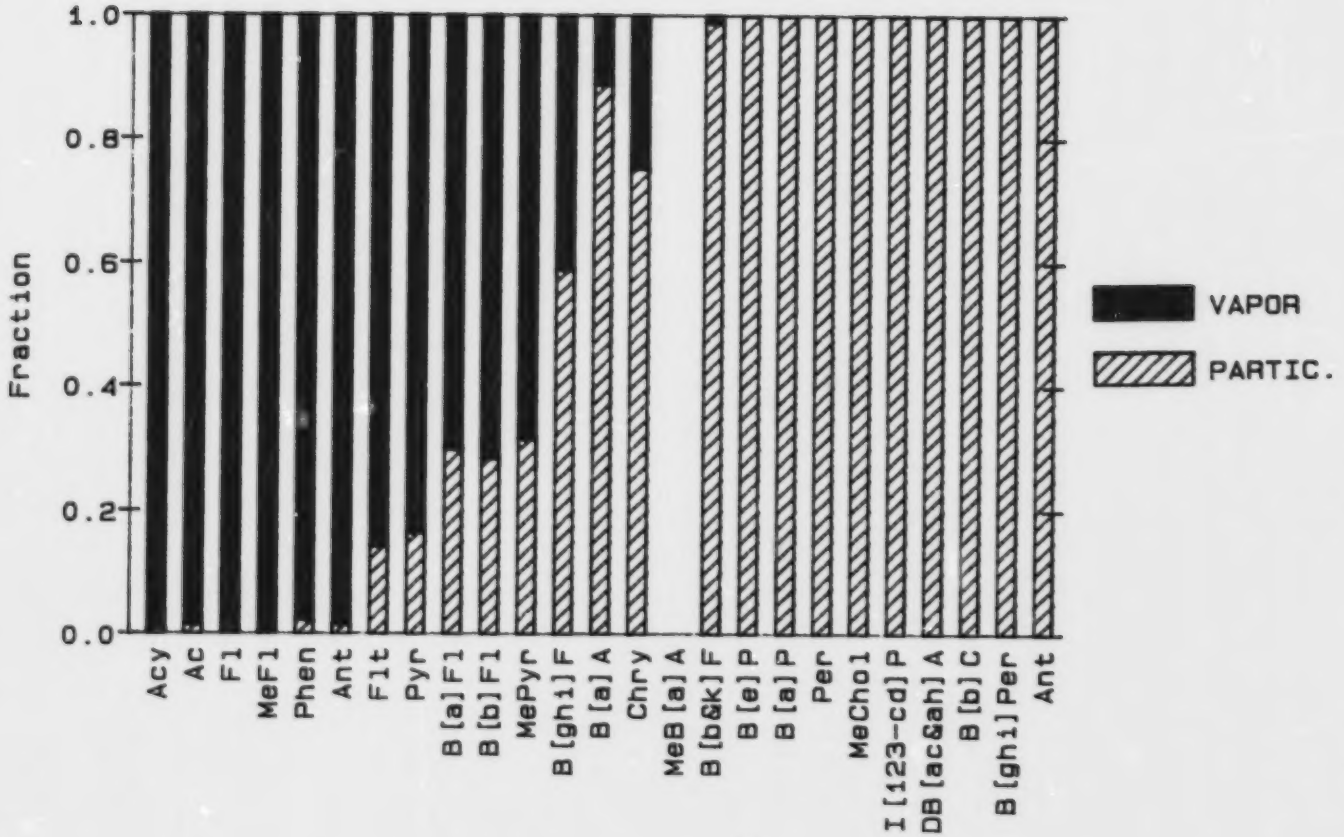

Figure 2: Mean Fraction of PAH Compounds Collected as Particulate or Vapor - Toronto

COMPOUNDS	MEAN	STD. DEV.	MEDIAN	MAX.	MIN.
Acenaphthylene*	14.05	19.21	5.99	93.05	0.22
Acenaphthene*	3.83	4.06	2.54	15.49	0.23
Fluorene*	9.99	7.76	6.80	31.19	1.73
2-Methyl-Fluorene	4.84	3.41	3.94	14.39	1.10
Phenanthrene	12.65	6.26	12.29	26.75	1.23
Anthracene	2.52	4.05	1.12	20.72	0.00
Fluoranthene	6.16	6.23	3.77	26.60	0.88
Pyrene	5.08	5.04	2.81	22.17	0.75
Benzo(a)Fluorene	1.11	1.32	0.58	6.19	0.00
Benzo(b)Fluorene	0.49	0.47	0.36	2.17	0.00
1-Methyl-Pyrene	0.35	0.41	0.29	1.63	0.00
Benzo(g,h,i)Fluoranthene	0.80	1.03	0.42	4.80	0.00
Benzo(a)Anthracene	0.90	1.36	0.21	6.15	0.00
Chrysene & Triphenylene	2.31	3.63	0.86	14.14	0.27
7-Methyl-Benzo(a)Anthracene	0.00	0.01	0.00	0.07	0.00
Benzo(b & k)Fluoranthene	3.27	5.27	1.15	21.90	0.32
Benzo(e)Pyrene	1.27	1.97	0.48	8.27	0.13
Benzo(a)Pyrene	0.64	0.97	0.21	4.09	0.00
Perylene	0.09	0.15	0.00	0.65	0.00
2-Methyl-Cholanthrene	0.00	0.00	0.00	0.00	0.00
Indeno(1,2,3-cd)Pyrene	0.95	1.28	0.40	5.09	0.09
Dibenzo(a,c) & (a,h)Anthracene	0.12	0.21	0.00	0.81	0.00
Benzo(b)Chrysene	0.12	0.27	0.00	1.12	0.00
Benzo(g,h,i)Perylene	1.19	1.41	0.61	5.85	0.12
Anthanthrene	0.07	0.19	0.00	0.87	0.00
TOTAL PAH	**72.82**	**56.37**	**49.59**	**212.88**	**14.88**

* Collection efficiency poor and dependent on ambient temperature (see text)

TABLE 3 - SUMMARY of VAPOR PLUS PARTICULATE PAH CONCENTRATIONS (ng/m^3) in MONTREAL (October 1984 - May 1986 - 29 Sampling Days)

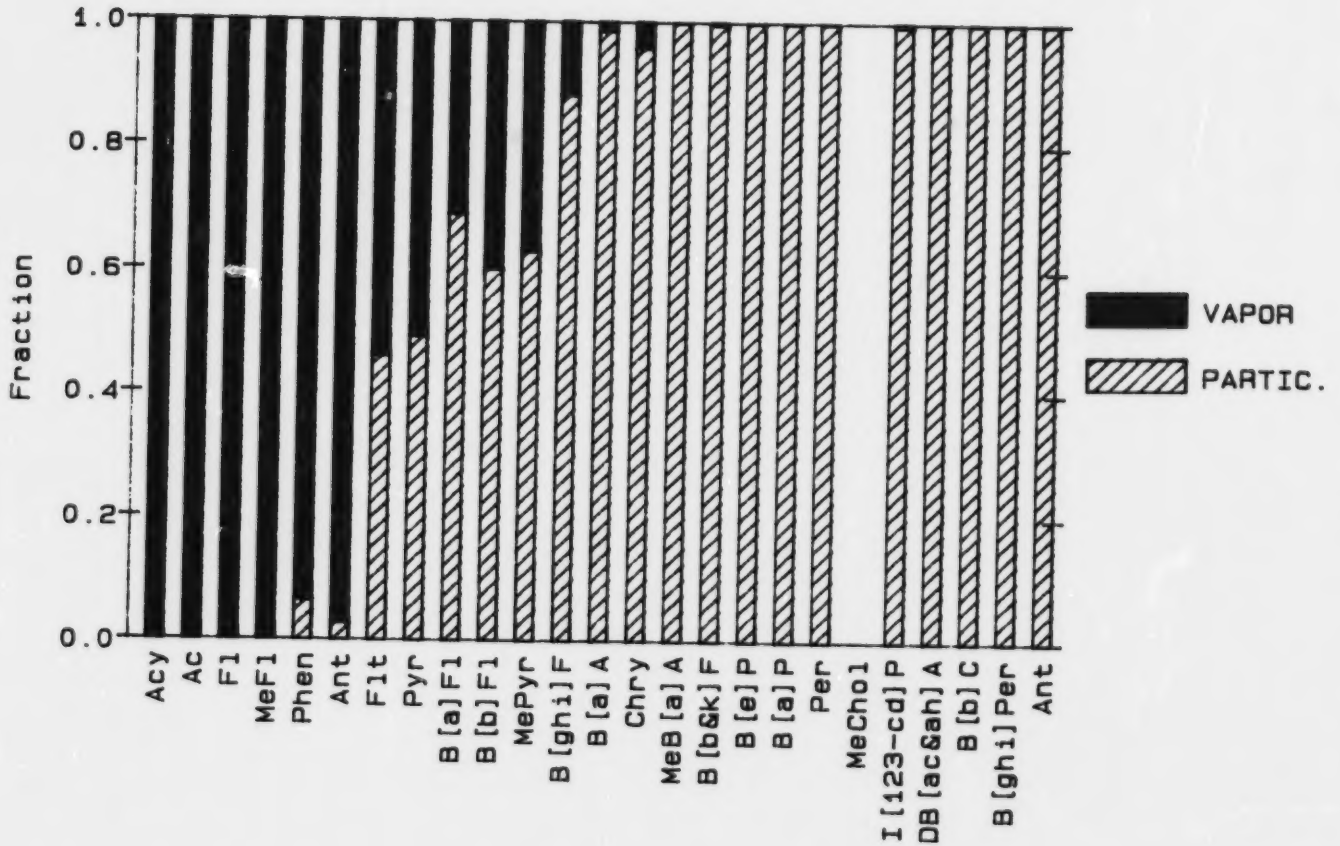

Figure 3: Mean Fraction of PAH Compounds Collected as Particulate or Vapor - Montreal

h, i)perylene at 1.2 ng/m^3. The mean concentration of benzo(a)pyrene was 0.6 ng/m^3 with a maximum measured concentration of 4.1 ng/m^3.

A comparison of mean vapor plus particulate concentrations of each PAH compound measured in Montreal and Toronto is given in Figure 4. Mean concentrations of all compounds except phenanthrene were higher at the Montreal site than at the Toronto site. Excluding acenaphthylene, acenapthene and fluorene, the mean total vapor plus particulate PAH concentration was 35.7 ng/m^3 in Toronto and 45.0 ng/m^3 in Montreal. PAH concentrations, with the exception of phenanthrene, showed little seasonal variation in Toronto. Phenanthrene concentrations were highest in the summertime. Generally, concentrations of the compounds found predominantly as vapors were highest in the spring and summer, while concentrations of compounds found as particulates were highest in fall and winter. In Montreal concentrations of almost all PAH compounds (both vapor and particulate) were highest in the fall and winter, although there were very few samples collected in the summer. Wintertime total PAH concentrations were significantly higher in Montreal than in Toronto.

Particulate PAH concentrations in Toronto in the winter months were much lower than those in Montreal. The mean particulate PAH concentration for spring and summer were similar at both sites, with Montreal fall concentrations approximately twice those of Toronto. Mean vapor PAH concentrations were similar at both sites with a winter/spring minimum and a summer/fall maximum. Phenanthrene showed the largest seasonal variation with a summer maximum of 25.5 ng/m^3 inToronto and 17.4 ng/m^3 in Montreal.

EMISSION SOURCES

General

Emissions of polycyclic aromatic hydrocarbons to the atmosphere result from the incomplete combustion of organic matter, ie. coal, oil, wood, gasoline and diesel fuel. In general, the less efficient the combustion process, the higher the PAH emission factor will be.[3] Although considerable attention has been focussed on PAH over the years and a good deal of effort has been devoted to the measurement of PAH emissions from a variety of sources, it is still difficult to quantify emission rates of PAH's to the atmosphere and a good deal of uncertainty exists over published emission factors for specific sources.

Because investigations typically measure only a small number of the total possible PAH compounds present in an emission source and because different investigations measure different subsets of PAH compounds, the use of total PAH emission estimates is subject to a great deal of error. Sampling schemes that only include particulate fractions will lead to an under-estimation of emissions depending on the concentration of vapor phase PAH present; vapor phase concentrations will, in turn, be dependent on the source and the sampling location at the source.[3]

Because of its carcinogenic potency, benzo(a)pyrene has been the most intensively studied PAH. Its presence has often been used as an indicator of other PAH's. Published emission factors for benzo(a)pyrene are usually in closer agreement than total PAH factors, however, the utility of benzo(a)pyrene emission estimates as a surrogate for total PAH is questionable. Benzo(a)pyrene often constitutes less than 1% of total PAH emissions and no consistent correlation has been found between it and other PAH's.[1,3,17] Recent work has shown that for a number of sources, extraction efficiencies of benzo(a)pyrene and other high

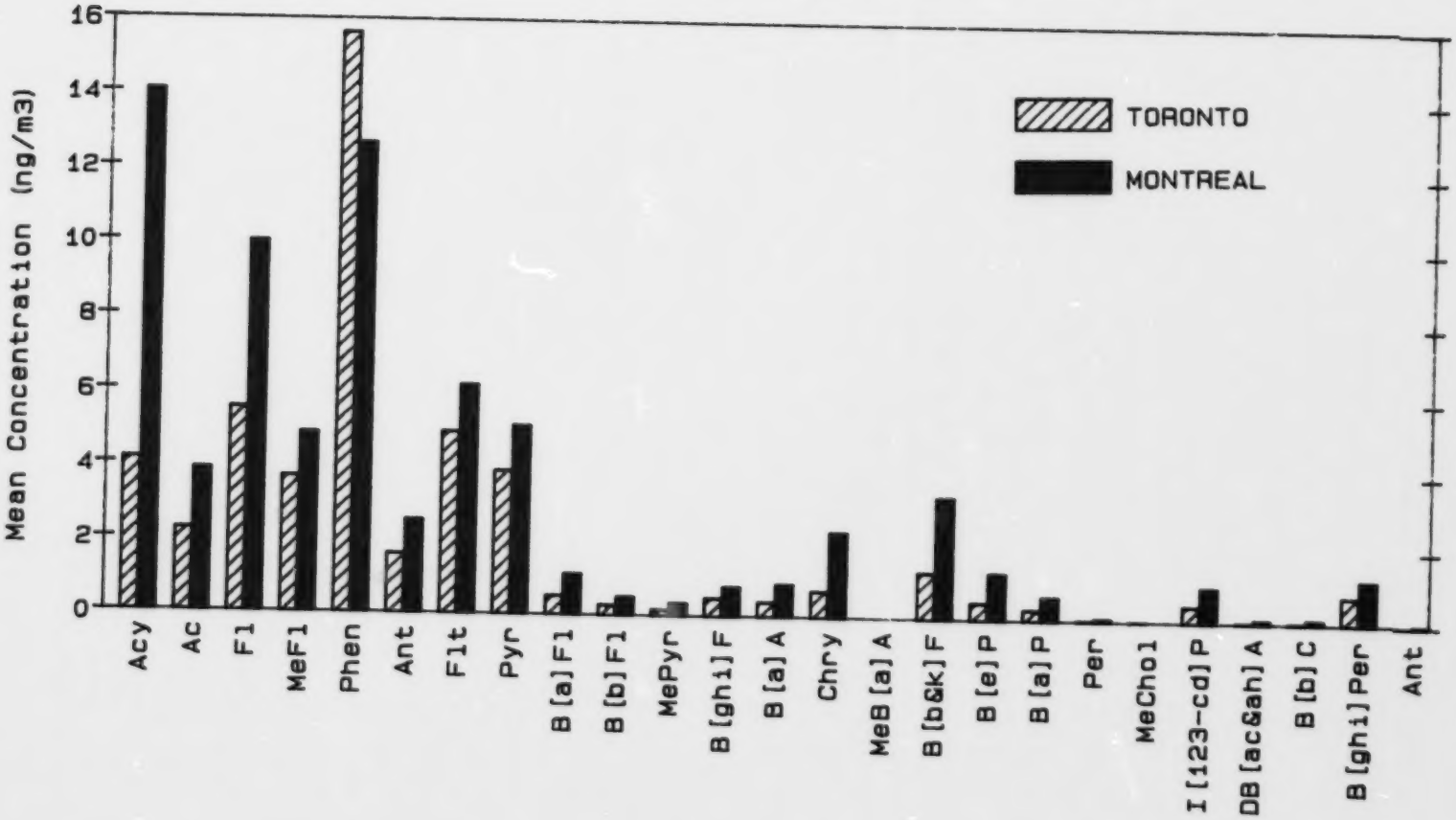

Figure 4: Mean Vapor Plus Particulate PAH Concentrations in Toronto and Montreal

molecular weight PAH from particulate matter can be poor using commonly employed extraction procedures.[17]

Even using consistent methodologies, measured emissions of PAH compounds may vary over several orders of magnitude for a particular source depending upon the age and condition of control equipment, combustion conditions and operating conditions.[3]

Published Emission Factors

"Total" PAH emissions are rarely defined in terms of species and are usually not comparable from one researcher to another. Derived emission factors show a great deal of variation even for benzo(a)pyrene. Part of this variation is explained by advances in control technology at some sources with earlier emission factors being much higher than recent factors derived from application of best available control technology. Emissions from coke production are a good example with the emission factor being dependent on the nature of the control system employed.

The quantity of PAH generated by a source varies with the efficiency of the combustion process. Insufficient combustion sources such as residential space heaters tend to emit higher amounts of PAH than do the better controlled, more efficient sources such as utility boilers. The concentration of PAH in fuel is of lesser importance than combustion conditions; although fossil fuels such as coal and oil contain substantial quantities of PAH, their combustion does not necessarily produce a higher emission level of PAH than wood.

In Table 4, a comparison of published emission estimates for benzo(a)pyrene and total PAH is given for the United States, Canada and Ontario. The percentage contribution of sources to benzo(a)pyrene or total PAH emissions is also given in the table. Total PAH emission estimates for the United States from three separate inventories were quite similar ranging from 8,400 to 11,000 Mg/y. The proportion of emissions due to specific sources showed greater variability. Only Ramdahl included aluminum smelting (25% of total) in his estimate. All three inventories estimated residential wood combustion (35 to 50% of total) and open burning (12 to 35% of total) to be major sources. Coke ovens were estimated to contribute $<1\%$ to 7% of total PAH emissions and transportation sources accounted for 3 to 20% of the total.

The three published benzo(a)pyrene emission estimates for the United States were not comparable with total benzo(a)pyrene emission estimates ranging from 170 to 1203 Mg/y. Two of the emission inventories are based on 1972-76 data and appear to over-estimate the contribution of coke ovens and under-estimate the contribution of residential wood combustion. The United States National Academy of Sciences (USNAS) inventory for 1972-1976 includes a much higher estimate (34%) of utility boiler emissions than the other inventories.

Neither of the two Canadian inventory estimates included residential wood combustion emissions. Both appear to use a high emission factor for coke ovens; it is not known whether this emission factor is based on the actual control technology employed at Canadian coke oven emission sources. The aluminum smelting industry appears to be a poorly characterized source and a true estimate of this industry's PAH emission contributions will have to await further emission studies.

The emission estimates in Table 4 are national or provincial totals. In urban areas which do not contain point sources such as coke ovens or aluminum smelters and which are not impacted by emissions from forest fires or agricultural burns, emission estimates would be quite different both in terms of magnitude of emissions and the percentage contribution of various sources. During the heating season, residential, commercial and industrial combustion sources will dominate

	UNITED STATES			UNITED STATES			CANADA	ONT
	TOTAL PAH			B(a)P			B(a)P	B(a)P
	A. LITTLE[18,19] (1978)	RAMDAHL[1] (1981)	PETERS[1] (1981)	A. LITTLE[19] (1978)	RTI[3] (1972-76)	USNAS[1] (1972-76)	LAO[1] (1982)	MOE[20] (1983)
Emission Estimate (Mg/y)	8,368	8422	11,031	170*	542	1283	20.5	19.1
Source Contribution (%)								
Coke Ovens	<1%	7%	6%	<1%	19%	15%	59%	63%
Aluminum Smelting	--	25	--	--	--	--	24	--
Residential Wood	58	45	35	42	12	3	--	--
Residential Coal	10	1	1	6	4	--	<1	--
Transportation	3	3	20	6	1	2	10	2
Open Burning★	24	12	35	35	59	43	--	35
Utility Boilers	1	5	1	1	<1	34	<1	<1
Petroleum Refining	<1	--	--	2	<1	--	4	
POTW	2	--	--	2	--		--	

* Intermediate Estimate ★ Including forest fires, agricultural burning, coal refuse fires -- Not included

TABLE 4 - COMPARISON of SOME RECENT EMISSION ESTIMATES for TOTAL PAH and BENZO(a)PYRENE in the UNITED STATES and CANADA

PAH emissions in urban areas. Depending on the amount of wood use, residential wood combustion emissions would be expected to be a major PAH source. The next most important source would be the transportation sector; this sector would also be expected to be the major PAH source during the non-heating season. In New Jersey, it was recently estimated that motor vehicles accounted for 98% of the state-wide non-heating season benzo(a)pyrene emissions while residential space-heating with wood accounted for 98% of the heating season emissions.[21] Winter emissions were estimated to be a factor of 50 higher than summer emissions although there was a good deal of uncertainty in the wood emission factors. Ambient measurements only showed a 4 to 6 fold increase in concentration from winter to summer.[21] A number of other researchers have established the dominance of transportation and oil and/or wood space heating as sources of PAH in typical urban areas.[22,23,24,25,26]

In areas with large point sources or a high density of residential wood fired appliances, PAH emissions and PAH ambient concentration levels would be expected to be greatly increased.

EMISSIONS of PAH in TORONTO and MONTREAL

No detailed emission inventory for PAH was available for Toronto and Montreal. However, from an analysis of the ambient data set, the following conclusions can be drawn.[16]

Toronto. Heating sources appear to be having only a small impact on measured PAH concentrations in Toronto. There was little variation in either the concentration of PAH or the ratio of their concentration to benzo(e)pyrene with season. The small variation in mean concentration or ratio of concentration of PAH to benzo(e)pyrene with wind direction indicated that there were no strong local sources of PAH. The excellent correlations between most PAH compounds (see Table 5) suggests that either the majority of the PAH compounds were originating from a single source or that most sources emit PAH with a consistent composition. Reported literature data on PAH profiles could not suppport the latter premise although there was overlap between source types. The most likely major contributor to PAH in Toronto is the automobile. Phenanthrene appears to have a unique source; because of its good correlation with temperature, an evaporative source is indicated.

Montreal. In Montreal, heating season sources had a large impact on measured particulate PAH levels although most of this impact was due to three very high concentration days during January 1985. A local residential wood combustion source was indicated on these days.[16] Ratios of PAH to benzo(e)pyrene were very similar to Toronto, despite the apparent influence of wood combustion (see Figure 5). Seasonal variations for most compounds were small as were variations with wind direction. Surprisingly, there appeared to be no significant increase in total PAH concentration when the site was downwind of the Montreal urban area. Correlations between most compounds were excellent at the Montreal site, again suggesting one major source or a common composition for all sources. The ratios of particulate PAH compounds to benzo(e)pyrene were not significantly different on the days with a suggested residential wood combustion impact than on days in other seasons. This indicates that distinguishing sources, based on ratios to benzo(e)pyrene, is a difficult task. A heating season contribution to PAH is indicated; the most likely source of non-heating season PAH emission is local

Compound	TORONTO				MONTREAL			
	Phenan-threne	Fluoran-thene	Benzo(b,k)-Fluoranthene	Benzo(a)-Pyrene	Phenan-threne	Fluoran-thene	Benzo(b,k)-Fluoranthene	Benzo(a)-Pyrene
Phenanthrene	1.0				1.0			
Anthracene	0.04				0.29			
Fluoranthene	0.63	1.0			0.45	1.0		
Pyrene	0.33	0.92			0.48	0.98		
Chrysene & Triphenylene	0.10	0.49			0.38	0.97		
Benzo(b&k)Fluoranthene	0.04	0.67	1.0		0.35	0.95	1.0	
Benzo(e)Pyrene	-0.02	0.66	0.99		0.35	0.95	0.99	
Benzo(a)Pyrene	-0.02	0.66	0.93	1.0	0.42	0.90	0.88	1.0
Indeno(1,2,3-cd)Pyrene	0.01	0.70	0.95	0.95	0.42	0.95	0.96	0.97
Benzo(g,h,i)Perylene	-0.00	0.70	0.93	0.95	0.42	0.93	0.92	0.99
Total PAH	**0.45**	**0.92**	**0.77**	**0.78**	**0.72**	**0.77**	**0.68**	**0.76**

TABLE 5: CORRELATION BETWEEN SELECTED PAH (Vapor plus Particulate) - TORONTO and MONTREAL

(For $n = 40$, $r_{025} \geq 0.30$)

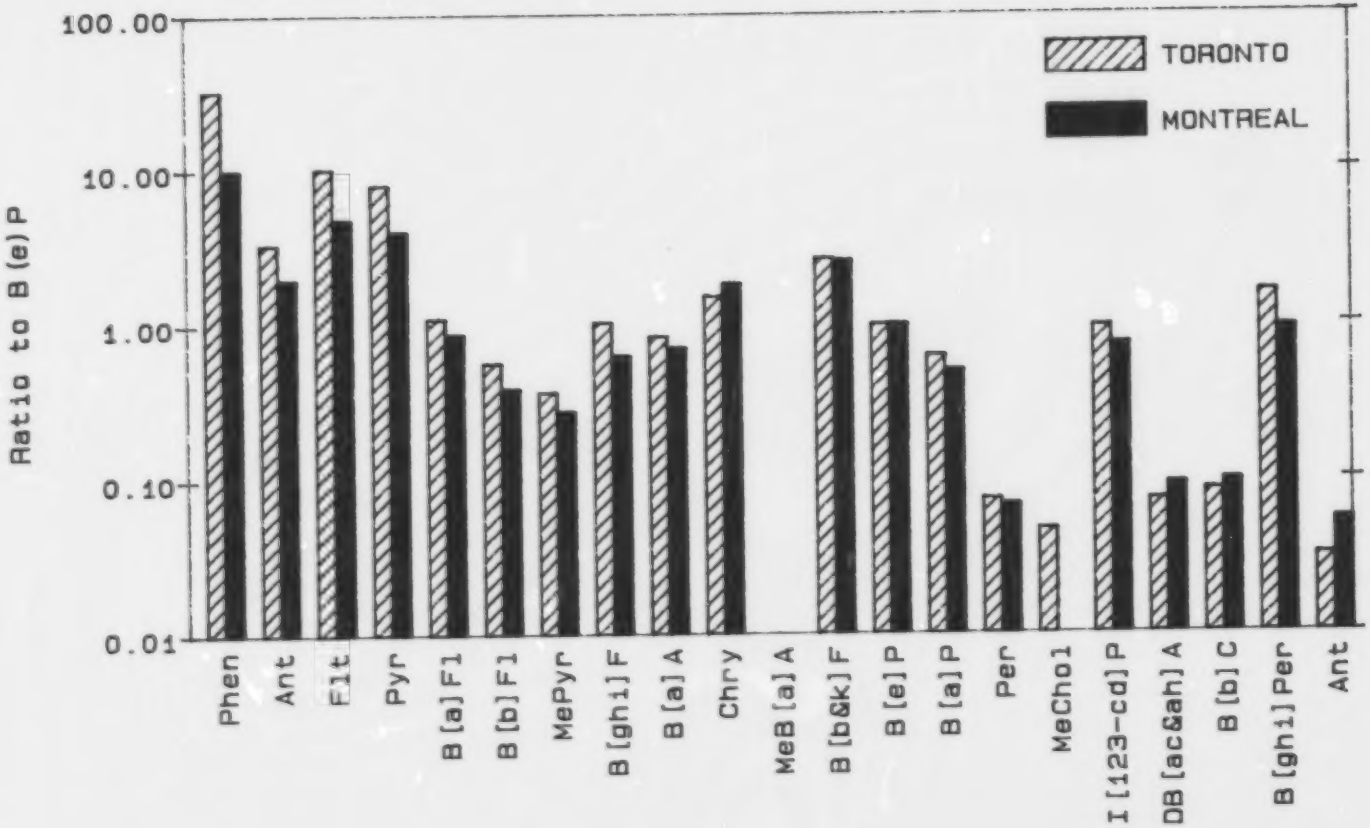

Figure 5: Mean Ratios of Vapor plus Particulate PAH to Benzo(e)Pyrene

automotive sources. As for Toronto, an evaporative source of phenanthrene is suggested.

DISCUSSION

Limitations on Data Analysis Imposed by Methodology

General. Data was collected in the form of twenty four hour averages on a six-day sampling schedule in Toronto and Montreal, although typically only every second sample was submitted for analysis. Data at both sites were available over an 18 to 20 month period, however, only the Toronto site had sufficient samples collected in each season for purposes of calculating a valid annual mean.

Since only one sampling site was utilized in each city, it is not possible to determine the representativeness of the measurement data re "typical" urban exposures to PAH, although as discussed later, the measurements are similar to those reported from United States urban areas. Based on emission and ambient data, mean PAH concentration levels would be expected to be higher at sites in the vicinity of point sources such as coke ovens or aluminum smelters or in locales with high residential wood usage.

As noted in the introduction, only a small subset of PAH compounds were measured in this program. The results then must be interpreted with caution, especially with regards to health effects. A number of other important categories of PAH and HAH have been shown to be present in urban air, many of which are known carcinogens.

Detection limits for individual compounds were approximately 0.06 ng/m^3 (for a typical 900 m^3 sample), values below detection were treated as 0.0 ug/m^3 for calculation purposes. Mean recovery of labelled PAH standards from filters and foams ranged from 75 to 85%; no corrections were made for recovery efficiency.

The hi-volume filter/PUF sampling system employed for this measurement program has been thoroughly studied by a number of researchers.[13,14,15] It has been found that measurements can be influenced by the following: (a) breakthrough and loss of volatile PAH from the PUF adsorbent; (b) "blow-off" or volatilization of particulate PAH from the filter to the PUF sorbent thus distorting "real" ambient particulate/vapor phase PAH distributions; (c) degradation/reaction of PAH on filters with inorganic gases such as ozone (O_3), nitrogen dioxide (NO_2), sulphur dioxide (O_2) and nitric acid (HNO_3) causing new compounds to be formed which are not detected by the analytical method. These degradation reactions have been shown to be dependent on temperature, humidity, reactive gas concentrations, particulates and PAH loadings, flowrate, light intensity and exposure time.

Most of the potential sampling and analytical errors will result in reported concentrations lower than those actually present in the sampled air.

Exposure and Potential Health Effects

PAH Carcinogenicity. Concern about PAH has resulted primarily from studies of their carcinogenic potential.[1,2,18,19] Most of these studies have been carried out by application of PAH compounds to the skin of mice; only limited results using other routes of exposure have been reported.[2] Complete reviews of the carcinogenicity bioassays of PAHs are available elsewhere.[27]

The International Agency for Research on Cancer (IARC) has evaluated selected polycyclics based on the overall weight of evidence of carcinogenicity to humans.[27] As noted in Table 6, 14 PAH and HAH compounds (6 of which were measured during

A. PROBABLE HUMAN CARCINOGENS

1. Benzo(a)anthracene*
2. Benzo(b)fluoranthene*
3. Benzo(j)fluoranthene
4. Benzo(k)fluoranthene*
5. Benzo(a)pyrene*
6. Dibenzo(a,h)acridine
7. Dibenzo(a,j)acridine
8. Dibenzo(a,h)anthracene*
9. 7H-dibenzo(c,g)carbazole
10. Dibenzo(a,e)pyrene
11. Dibenzo(a,h)pyrene
12. Dibenzo(a,i)pyrene
13. Dibenzo(a,l)pyrene
14. Indeno(1,2,3-cd)pyrene*

B. POSSIBLE HUMAN CARCINOGENS

1. Anthanthrene*
2. Benz(c)acridine
3. Carbazole
4. Chrysene*
5. Cyclopenta(c,d)pyrene
6. Dibenz(a,c)anthracene*
7. Dibenz(a,j)anthracene
8. Dibenzo(a,e)fluoranthene
9. 2 and 3-methyl fluoranthene

* Measured during this sampling program

TABLE 6 - IARC LIST of PROBABLE and POSSIBLE PAH HUMAN CARCINOGENS

this program) are judged to be probable human carcinogens and another 9 compounds (3 measured) were rated as possible human carcinogens. Fluoranthene, pyrene, benzo(g,h,i)perylene and benzo(e)pyrene may be important co-carcinogens. Phenanthrene is considered a suspect carcinogen by the National Institute for Occupational Safety and Health (NIOSH).[28]

Thus, of the PAH compounds measured, 13 were judged to be of most importance from a health effects point of view. The mean and maximum concentrations of these 13 compounds are shown in Table 7 for Toronto and Montreal. Of the probable/possible human carcinogens, benzo(b&k)fluoranthene were found in the highest concentrations at both sites. Of compounds considered co-carcinogens or mutagens, fluoranthene and pyrene were found in the highest concentrations overall at both sites. Mean and maximum concentrations of all the compounds in Table 7 were higher at the Montreal site than the Toronto site. The mean of the sum of the concentration of the 13 compounds potentially important as human carcinogens was 13.4 ng/m^3 at the Toronto site and 22.1 ng/m^3 at the Montreal site.

COMPOUND	TORONTO		MONTREAL	
	Mean	Maximum	Mean	Maximum
1. Fluoranthene	4.9	13.2	6.2	26.6
2. Pyrene	3.9	14.6	5.1	22.2
3. Benz(a)Anthracene	0.4	5.8	0.9	6.2
4. Chrysene + (Triphenylene)	0.7	3.4	2.3	14.1
5. Benzo(b)Fluoranthene and 6. Benzo(k)Fluoranthene	1.3	8.2	3.3	21.9
7. Benzo(e)Pyrene	0.5	3.4	1.3	8.3
8. Benzo(a)Pyrene	0.3	3.1	0.6	4.1
9. Indeno(1,2,3-cd)Pyrene	0.5	3.7	1.0	5.1
10. Dibenz(a,c)Anthracene and 11. Dibenz(a,h)Anthracene	0.04	0.5	0.1	0.8
12. Benzo(g,h,i)Perylene	0.8	6.6	1.2	5.9
13. Anthanthrene	0.02	0.2	0.1	0.9
Sum of Above 13 PAH Compounds	**13.4**	**58.8**	**22.1**	**109.1**

TABLE 7: MEAN and MAXIMUM CONCENTRATIONS (ng/m3) of PAH COMPOUNDS which are PROBABLE or POSSIBLE HUMAN CARCINOGENS or are CO-CARCINOGENS

Twenty-eight individual PAH compounds were measured during this study. As discussed in the introduction, these compounds represent only a small fraction of the hundreds of polycylic organic compounds that might be present in ambient air. Because of the complexity of identifying and quantifying all components of organic particulate matter in air and determining potential health effects of each component through animal tests, etc., alternate approaches have been attempted. Many of these approaches rely on a fractionation scheme which divides collected particulate matter into fractions containing known classes of compounds, for example - non-polar, moderately polar and polar fractions. The extract or extract fractions are then submitted to a short term bacterial mutagen assay (also referred to as genotoxicity testing) or Ames testing.[29,30] Mutagenic assays of particulate matter may be a practical alternative to current PAH identification and quantification activities.

Existing/Proposed Air Quality Criteria for PAH. Pollutants for which no formal air quality criteria have been adopted are usually referred to as non-criteria air pollutants. For most organic air pollutants including PAH, few agencies have adopted air quality standards. The U.S. EPA has taken a restrained role in the development of regulatory and environmental standards for the control of non-criteria air pollutants.[31]

The most common approach used to assess the significance of measured levels of organic pollutants in air is to compare them to threshold limit values (TLV's) corrected for non-occupational environments.[32,33] In the United States, over 20 state and local agencies use TLV's to regulate non-criteria air pollutants.[33] Despite the fact that the American Conference of Government and Industrial Hygienists (ACGIH) states that TLV's should not be applied to non-occupational environments, the TLV approach is attractive because it is applicable to hundreds of substances and regulatory agencies do not have to obtain the environmental and health information that other approaches may require.[33]

Another common approach to deriving acceptable concentration ranges for compounds in ambient air is to use quantitative risk assessment methodology.[34] This approach is most applicable to carcinogens and requires an estimate of a compound's carcinogenic potency expressed as a unit risk value. A unit risk is the excess lifetime risk due to a continuous/constant lifetime exposure to one unit of concentration.[34] For air pollutants, unit risk values are usually expressed in terms of $\mu g/m^3$ or ng/m^3 of the pollutant in air. The unit risk approach assumes that dose-response curves derived from animal studies are linear at low doses.[34] Risks are normally upper-bound estimates. Risks may be reported in terms of risk for an individual or risk for an exposed population (aggregate risk). Maximum individual risks are derived by multiplying the unit risk factor for the specific chemical of concern by the highest exposure estimate in the area under examination. Aggregate risks are derived by multiplying the number of people exposed times the expected exposure concentration times the unit risk value.[34] Uncertainties are inherent in quantitative risk assessment because of assumptions required to extrapolate from high dose studies to low dose situations and because of the statistical modelling techniques required to fit data points. Unit risk factors are considered plausible, upper bound estimates of risk; true risks are not likely to be higher than the estimate. Acceptable upper bound incremental cancer risks are usually in the one in a million (10^{-6}) to one in a hundred thousand (10^{-5})range.[35]

In most risk assessment approaches for PAH, benzo(a)pyrene is used as a surrogate for total PAH or more commonly for total polycyclic organic matter (POM). POM at times is referred to as products of incomplete combustion or PIC. As

previously noted, benzo(a)pyrene concentrations are often used as a surrogate for total PAH or total POM. There are several key limitations to using benzo(a)pyrene to represent exposures to a complex mixture of compounds. A major weakness in using the potency estimates derived from occupational studies is the mix of POM in the exposures studies (coke oven emissions, roofing tar fumes and gas fumes) almost certainly differs from ambient air. Relationships between benzo(a)pyrene and other POM are also complicated since synergistic and antagonistic effects are known to occur. Benzo(a)pyrene is almost certainly not a stable indicator of the carcinogenicity of polluted air, however, no better alternatives for its use presently exist. In both Montreal and Toronto benzo(a)pyrene was well correlated with other potentially carcinogenic PAH.

In Table 8, a comparison of maximum individual risks for benzo(a)pyrene, PIC and a number of other organics[36] measured at the same site in Toronto and Montreal are presented. PIC represented by benzo(a)pyrene concentrations has the highest calculated maximum individual risk value of the compounds studied. Since the Toronto and Montreal sites are currently the only ones in Canada with a long term data record, it is not known if these results would be applicable to other urban areas.

Compound	Unit Risk	Highest Mean Concentration ($\mu g/m^3$)	Maximum Individual Risk
Benzo(a)Pyrene	3.3 x 10-3	6 x 10-4(a)	2 x 10-6
PIC*	0.42	6 x 10-4(a)	2.5 x 10-4
Benzene	6.9 x 10-6	21.5(a)	1.5 x 10-4
Tetrachloroethylene	1.7 x 10-6	2.5(b)	4.3 x 10-6
Trichloroethylene	4.1 x 10-6	1.8(b)	7.4 x 10-6
Carbon Tetrachloride	1.5 x 10-5	1.1(a,b)	1.7 x 10-5

* Benzo(a)pyrene used as surrogate (a) Montreal (b) Toronto

TABLE 8: COMPARISON of CALCULATED MAXIMUM INDIVIDUAL RISKS for BENZO(a)PYRENE, PIC and OTHER ORGANICS BASED on MONITORING DATA from TORONTO and MONTREAL

Comparison of Toronto and Montreal PAH Concentrations with those Reported from other Locations. The thirteen PAH compounds classified as suspect carcinogens were measured during three Canadian surveys conducted in the vicinity of specific PAH sources: Whitehorse, YT - residential wood combustion;[5] Sydney, N.S. - coke ovens;[6] and Kitimat, B.C. - aluminum smelter.[7] In Table 9, the mean concentrations of PAH (vapor plus particulate) measured during these surveys are compared to those measured in Montreal and Toronto. Although the other studies were of short duration, it is quite apparent that PAH loadings in the vicinity of emission sources can be much higher than those in typical urban areas.

A large body of information has been reported in the literature on PAH loadings in urban areas.[1,3,4,21,22,23,25,30,37,38,39] However, relatively few of the surveys

Compound	Montreal, Quebec (n = 29)*	Toronto, Ontario (n = 42)	Kitimat, B.C. (n = 3)	Whitehorse, YT (n = 8)	Sydney, N.S. (n = 20)
Fluoranthene	6.2	4.9	144.7	34.0	9.6
Pyrene	5.1	3.9	86.8	39.9	8.0
Benzo(a)Anthracene	0.9	0.4	7.9	8.3	1.6
Chrysene &Triphenylene	2.3	0.7	26.2	11.5	2.3
Benzo(b & k)-Fluoranthene	3.3	1.3	17.2	10.7	3.0
Benzo(e)Pyrene	1.3	0.5	6.7	4.3	1.5
Benzo(a)Pyrene	0.6	0.3	14.1	8.9	1.3
Indeno(1,2,3-cd)Pyrene	1.0	0.5	2.7	6.0	1.2
Dibenzo(a,c) & (a,h)Anthracene	0.1	0.04	1.3	2.2	0.5
Benzo(g,h,i)Perylene	1.2	0.8	3.4	5.6	1.4
Anthanthrene	0.1	0.02	0.8	--	--

* No of Sampling Days

TABLE 9: REPORTED PAH (VAPOR plus PARTICULATE) RESULTS (ng/m^3) from CANADIAN SAMPLING SITES

have been long term and very few have utilized a backup vapor phase collection system. In Table 10, mean concentrations of PAH compounds measured in various cities in the United States and Europe are compared to those measured in Montreal and Toronto. The number of samples collected, the duration of the sampling program and the literature reference are given in the table. The Montreal and Toronto results are quite similar to those recently reported for many urban areas in the United States and Europe.

Benzo(a)pyrene is the only PAH compound for which a substantial historical data base exists. Table 11 contrasts recently reported (1977-84) benzo(a)pyrene concentrations with those reported from Canadian and U.S. cities in the period 1958 to 1976. It is evident that mean concentrations have fallen dramatically from the 1950's and 1960's but only a modest decline has been realized since the mid 1970's.

7 SUMMARY and CONCLUSIONS

The hi-vol based filter/PUF sampling system performed well during the course of the measurement program. Collection efficiencies were excellent for three to six ring PAH compounds with poor collection efficiency for two ring compounds. Particulate/vapor phase distributions were quite predictable and agreed well with distribution data published by others. Concern over sampling losses due to chemical rearrangement and degradation of PAH may be overstated.

Of the PAH compounds considered probable or possible carcinogens benzo(b,k)fluoranthene was found in the highest concentration at both sites. During the measurement period, mean PAH concentrations were higher in Montreal than in Toronto.

Sources of PAH are still poorly characterized. The use of ratios of PAH compounds to benzo(e)pyrene was not a good source identification tool in either Toronto or Montreal. Most of the PAH compounds were highly correlated with one another and in both these cities benzo(a)pyrene concentrations could be used to estimate total PAH concentrations. A unique souce of phenanthrene was indicated in both cities; because of phenanthrene's good correlation with temperature, an evaporative source was indicated.

Using current estimates of carcinogenic risk associated with organic air pollutants, measured levels of benzo(a)pyrene (as a surrogate for PIC) represent the highest risk of the organic compounds (both volatile and semi-volatile) recently measured in Toronto and Montreal. This is despite the fact that benzo(a)pyrene levels have been reduced greatly over the past twenty to thirty years.

As for most toxic air pollutants, the ambient air data base for PAH is very sparse. Additional long term monitoring in urban areas of Canada is required. Since PAH levels can be significantly higher near point source emitters, monitoring should also be conducted in residential areas in the vicinity of aluminum smelting and coke oven operations. Additional data is also required on other components of polycyclic organic matter including nitro PAH, oxygenated PAH and heterocyclic aromatic hydrocarbons. The use of routine mutagenicity testing of urban particulate matter should also be considered as a supplement to conventional PAH monitoring.

City	No. of Samples	Sampling Period	Mean Concentration (ng/m³)				Reference
			B(a)A	B(b&k)F	B(a)P	B(g,h,i)Per	
Toronto, Ont.	42	Aug.84-Jul.86	0.4	1.3	0.3	0.8	--
Montreal, PQ	29	Oct.84-May 86	0.9	3.3	0.6	--	--
Los Angeles, CA	~ 1000	Aug.81-Mar.82	0.5	1.3	0.6	--	39
Newark, NJ	16 - 35	Winter 1982	1.4*	2.3*	1.6*	2.7*	21
Newark, NJ	27 - 38	Summer 1982	0.2*	0.5*	0.2*	0.3*	21
Vancouver, B.C. (Downtown Site)	14	Feb.85-Mar.85	0.4	1.3	0.3	2.2	38
Stockholm, Sweden (11 sites)	~200	Jun. 80-Dec.1983	0.5	--	1.6	5.4	23
Columbia, SC	13	Feb.81-Apr.83	--	--	0.5	--	8
Kokkola, Finland	11	May 85-Nov.85	0.7	--	0.6	0.9	37

* Geometric Mean

TABLE 10: MEAN CONCENTRATIONS of BENZO(a)ANTHRACENE, BENZO(b,k)FLUORANTHENE, BENZO(a)PYRENE and BENZO(g,h,i)PERYLENE in TORONTO, MONTREAL and OTHER SELECTED CITIES

City/Area	No. of Samples	Sampling Period	Mean Concentration ofB(a)P (ng/m^3)	Reference
RECENT				
Toronto, Ont.	42	Aug.84-July 86	0.3	--
Montreal, PQ	29	Oct.84-May 86	0.6	--
Newark, NJ	137	July 81-Feb.83	0.8*	21
Los Angeles, CA	~1000	Aug.81-Mar.82	0.6	39
U.S. (49 urban and suburban sites)	--	1977-1982	0.5	40
HISTORICAL				
Toronto, Ont. (Lawrence/Kennedy)	20	Apr.75-Mar.76	1.1	41
Hamilton, Ont.	20	Apr.75-Mar.76	2.3	41
Chicago, IL	Annual Avg.	1975	1.0	4
Youngstown, OH	Annual Avg.	1970	7.1	4
Canada (Avg. of 10 Towns)	--	1971-1973	0.8	4
Welland, Ont.	--	1971-1973	7.0	4
Urban U.S.A. (Avg. of 10 sites	--	1958-1959	13.3	4

TABLE 11: AMBIENT BENZO(a)PYRENE CONCENTRATION in CANADIAN and U.S. URBAN AREAS RECENT and HISTORICAL

8 ACKNOWLEDGEMENTS

The contributions of the following are greatfully acknowledged: C. Chiu, K. Li, M. Lanoy and P. Howes, Analytical Services Division, Ottawa; J. Mar and D. Wang, Pollution Measurement Division, Ottawa; R. Allard, Communauté Urbaine de Montréal, Montreal; F. Austin, Ontario Ministry of the Environment.

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THE ENVIRONMENTAL IMPACTS OF EMISSIONS FROM RESIDENTIAL COMBUSTION HEATING SYSTEMS IN CANADA

J.H. Kozak
Environment Canada
Dartmouth, Nova Scotia

INTRODUCTION

Until 1973, oil was the primary fuel for residential heating in Canada. Since then, a combination of factors, but most importantly the world energy crises has resulted in a shift to the use of natural gas, wood, kerosene, propane and electricity for residential heating. In addition, the federal government encouraged this shift by a limited grants program to assist homeowners in the substitution of other heating fuels for oil.

At the present time, the two most widely used fuels for domestic heating in Canada are natural gas and electricity, with oil ranking third. Table 1 shows this trend for the period of 1973 to 1986. In most regions, decreases in oil use was offset by increased electricity usage, but there was also a noticeable increase in wood use, especially in the Atlantic provinces. It should be noted that these figures may underestimate the energy provided by wood since it does not represent the use of wood for supplementary or recreational purposes.

The indications are that the trend towards increased use of so-called solid fuels (wood in particular) for home heating gained greater momentum in the early 1980's and is expected to continue into the foreseable future. As a result of environmental concerns raised in many mid and Western states in the United States and increased complaints regarding air quality in many localities in Canada, the National Research Council's Associate Committee on Scientific Criteria for Environmental Quality formed a panel to review the environmental and health impacts (indoor and outdoor) of residential combustion heating systems. The objectives of the NRC panel were to;

- collate and assess the basic scientific criteria relevant to the problem;
- bring together findings regarding the emission levels from various combustion appliances used in residences; and
- provide a succinct outline of the environmental and health impacts of residential combustion appliances.

However, because of federal budget cuts in 1984, the NRC Associate Committee was terminated in March 1985. As a result, the panel was disbanded and the work stopped upon the completion of a preliminary draft report in mid 1985.

After considerable discussion, Environment Canada decided to complete the report under contract, but because of its mandate, to focus on the outdoor environmental impacts and to investigate the source control strategies to reduce any of the impacts noted. A final report was completed by the contractor in mid 1987 and is undergoing revisions suggested by provincial and federal government reviewers. An Environment Canada manuscript report should be available for distribution in the spring or summer of 1988.

The intent of this paper is to review the final contractor report (1),

with emphasis on residential wood combustion and toxic emissions such as polycyclic aromatic hydrocarbon (PAH) compounds and fine particulates.

RESIDENTIAL COMBUSTION SOURCES

In the initial review, the NRC panel decided to assess the impacts of all types of residential combustion heating systems. However, early on in the panel review, it was recognized that residential wood combustion was the major area for concern in Canada, as well as in the United States. Therefore, the NRC and Environment Canada's consultant report focussed on the impacts and controls associated with residential wood combustion.

It is worth briefly reviewing why and how this focus developed. The fuels used for residential heating can be divided into two categories - solid and liquid/gaseous. In Canada, the main solid fuels are wood and coal, with the latter being a minor fuel in most parts of the country.

First of all, there are two types of emissions of concerns from the combustion of all hydrocarbon fuels, those arising from incomplete combustion and those that result from normal combustion processes. Products of incomplete combustion include various gaseous hydrocarbons, particulates, carbon monoxide and other elements and heavier molecular weight compounds such as polynuclear organic matter (including PAHs). Combustion products include carbon dioxide, water vapour, sulphur dioxide and nitrogen oxides.

Overall quantities of emissions are directly related to the amount of fuel consumed and the efficiency of the combustion system. Emission factors for the various combustion system have been developed and some of these are listed in Table 2. It can be seen from this comparison that on an heat input basis, with the exception of sulphur dioxide, wood stoves produce dramatically higher levels of volatile organic compounds, carbon monoxide, particulate matter and POMs (i.e. 50-1200 times depending on the compound compared to oil) than natural gas and oil residential heating systems.

Secondly, based on a 1980 national air emission inventory, as shown in Table 3, carried out by Environment Canada, residential combustion sources are relatively small compared with emissions from the transportation and stationary industrial sources. However, it must be kept in mind that residential combustion sources may have their impact magnified because of the density of the units in an urban area, the low elevation of the emission source, the low temperature of stack gases, and meterological topographical and building effects.

Table 4 specifically deals with emissions from residential fuel combustion in Canada for 1985 based on unpublished data from Environment Canada and consultant studies. Although, wood represents approximately 6% or so of the households heating requirements in Canada, residential wood combustion (RWC), accounts for significant portions of particulate matter (97%), CO (97%), hydrocarbons (95%), VOC (97%) and PAH (73%) emissions from all residential combustion sources.

Thirdly, based on a study (2) done for Energy, Mines and Resources Canada, using local wood use statistics and climatological data, a number of urban areas in Canada were indicated to have potential air quality problems due to RWC activities. A number of ambient and source modelling studies in the United States also suggested health concerns associated with RWC emissions.

Also, a study (3) completed for Energy, Mines and Resources Canada, on the viability of using wood for domestic heating, suggests that RWC is not a fad, and that the current level of wood use will be maintained or increased in the future.

Finally, in terms of air pollution emissions both natural gas and fuel oil furnaces are at the stage where available high efficiency models are at the optimum for fuel efficiency and therefore reduced emissions. Whereas, wood stoves are operator dependent and are still undergoing changes which could result in improved efficiencies and air emissions reductions. Therefore, RWC holds the greater potential for further air emissions reductions in the future across Canada.

ENVIRONMENTAL IMPACTS

Since 1970, the National Air Pollution Surveillance Network (NAPS), a co-operative effort among the federal, provincial and several municipal governments has routinely measured air quality in the largest urban centres across Canada. The NAPS network is of limited value in measuring the specific impacts from residential combustion heating sources, but it is still of interest to note the improvement in air quality (4) in the major urban centres across Canada, as noted in the following table:

Pollutant	1985 Mean levels	Percent Decline from 1974 level	Attainment Rate for Acceptable Level (%)							
			Annual		1 hour		8 hours		24 hours	
			1974	1985	1974	1985	1974	1985	1974	1985
SO_2	6 ppb	54	82	100	87	92	--	--	85	95
NO_2*	22 ppb	29	96	100	86	100	--	--	84	96
CO	1.0 ppb	58	--	--	97	98	71	94	--	--
O_3*	17 ppb	no trend	50	40	18	49	--	--	--	--
TSP	42.9 ug/m^3	45	51	98	--	--	--	--	--	--

* For NO_2 and O_3 the attainment rate is compared to 1977 to 1979 respectively.

The NAPS system does not routinely measure trace organics but mainly criteria air pollutants and is operated in the larger Canadian urban centres rather than smaller urban centres or rural areas where the influence of RWC emissions would be more prevalent.

In attempting to assess the impacts of residential combustion devices, a literature review of ambient air studies specifically dealing with residential combustion sources and source apportionment studies was undertaken. It was noted early in both NRC and the contractor reviews that there were very few studies related to the air quality impacts of emissions directly related to residential combustion devices except for residential wood combustion. In terms of potential impacts, the focus was placed on RWC and divided into non-biological or nuisance impacts and biological effects.

Biological Impacts

No direct cause and effect relationship between residential wood

combustion emissions outdoors and health has been determined to date. However, based on the measured emissions from wood stoves and a number of ambient air studies done to date, there is a legitimate concern for potential health impacts. As noted earlier, the contractor's report deliberately focussed on outdoor impacts and the indoor impacts are beyond the scope of this paper. But, there is a need to address the outdoor and indoor air quality relationships associated with residential wood combustion, since the latter may be much more significant in terms of total human exposure to toxic air pollutants.

In 1980, Cooper's paper (5) highlighted the need for a close look at RWC emissions, since the chemical products formed during wood combustion are very numerous and diverse; and include many toxics compounds such as:

- 17 priority USEPA pollutants
- up to 14 carcinogenic compounds
- 6 cilia toxic and mucus coagulating agents
- 4 co-carcinogenic (i.e. initiating or cancer promoting agents)
- many other toxic gases such as carbon monoxide, and respiratory irritants such as aldehydes and phenols.

In addition, it has also been determined that a large percentage of woodsmoke total suspended particulate matter (TSP) emissions are in the fine or respirable range (RSP). The respirable suspended particulates are particles of less than 3.5 μm in diameter and tend to be carried into and lodge in the deepest part of the lungs during breathing.

Also, dioxins and furans have been identified (6) in chimney and bottom ash particulates of residential wood combustion units, both in the United States and Ontario. It is interesting to note that the U.S. work was associated with wood treated with herbicides whereas the Ontario study was for untreated woods. Although, not conclusive in terms of dioxins and furans emissions in stack emissions, it does warrant further investigation.

To date, most ambient/source apportionment studies for RWC emissions have evaluated particulate matter (total and respirable) and polycyclic aromatic hydrocarbons (PAH), in particular benzo(a)pyrene (BaP). It is not the intention of this paper to review all the studies done in the U.S. but rather to highlight several to indicate the nature of the RWC impacts. It should be kept in mind that recent U.S. data suggests that average BaP levels in urban centres are less than 1 $ng.m^{-3}$, with the average slightly higher in the wintertime. Some of the studies (1) indicated the following;

.Medford, Oregon - RWC was considered to be largest contributor to measured TSP (31%) and RSP (66%), and sampling indicated that maximum TSP from RWC was 126 $\mu g.m^{-3}$ over 12 hours.

. Telluride, Colorado - Where 25% of residential heating is by RWC, showed a mean BaP level of 7.4 ngm^{-3} at one site.

.Peterville, Alabama - BaP levels on occassion, exceeded background concentration by as much as 80 ngm^{-3}. BaP measurements included both gaseous and particulate PAHs.

. U.S. Pacific Northwest (1980 - 1981) - Eight urban centres were monitored for TSP, BaP and particle size, chemical receptor modelling showed that RWC emissions represented 16.7 to 84.7 μgm^{-3} of the TSP levels and 45% to 93% of the fine particle mass. Mean BaP concentrations were 4.1 ngm^{-3} compared with a mean background of 0.4 ngm^{-3}.

. Portland and Medford Aerosol Characterization - This study indicated that as much as 36% and 86% of the fine particle mass measured in Portland and Medford, respectively could be attribured to RWC emissions.

. Waterbury Vermont (January and March, 1982) - Ambient air monitoring conducted in this rural community with 50% of residential heating requirements supplied by RWC, showed that 60-70% of TSP was composed of RSP. Nephelometer measurements suggested short term nighttime TSP levels could be 5-10 times higher than afternoon levels.

In Canada, the major ambient air study done in conjunction with residential wood combustion emissions was in Riverdale, a subdivision of Whitehorse in the Yukon Territory. The Riverdale area is located in a basin and over 50% of the homes burn five cords of softwood per year. This, in combination with the stable air masses of the northen interior, results in very high TSP loadings. At one site, TSP levels exceeded 550 $\mu g.m^{-3}$, with means of 130 and 138 $\mu g.m^{-3}$ for the winters of 1982 and 1983, respectively. The RSP was estimated to account for 95% of the particulate mass, and chemical receptor modelling suggests that 90% of the particulate arose from residential wood combustion. Although the PAH measurements may not be representative of average levels as a result of selecting the worst-case situations, it is noteworthy that BaP levels exceeded 10 $ng.m^{-3}$ on occasion. Also, at two of three sites, BaP concentrations in excess of 44 $ng.m^{-3}$ were measured.

Preliminary air quality and residential wood combustion investigations in Truro and Lower Sackville in Nova Scotia from February to April, 1984, during a relatively mild and unstable weather conditions, indicated low average TSP levels not exceeding 22 $\mu g.m^{-3}$. The two communities studied had residential wood combustion activity exceeding 45%, and were located in shallow river valleys with no major industries. It was noted that RSP accounted for about 55% of the TSP. Average BaP levels in both centres were less than 0.35 $ng.m^{-3}$. TSP levels measured at three sites in Lower Sackville during a colder winter, December 1984 - March 1985, were considerably higher, averaging between 30.8 and 39.8 $\mu g.m^{-3}$. A peak level of 122.9 $\mu g.m^{-3}$ was recorded at one site, the highest level ever recorded in the Halifax-Dartmouth area. It was estimated that, on average, wood smoke accounted for more than half the TSP measured.

TSP sampling done in Fredericton in January-February 1985, showed TSP levels at two sites with high RWC activity, averaged between 31-34 $\mu g.m^{-3}$, while a control site averaged 19 $\mu g.m^{-3}$. Particle sizing was typical of wood smoke.

Carbon monoxide is also of concern due to the large CO emissions from wood combustion relative to other fuels. However, in Whitehorse, measured CO levels during high TSP recordings in the Riverdale area were lower than those measured at the downtown NAPS station.

Non-biological Effects

The most commonly non-biological or nusiance impacts associated with RWC emissions are odours, soiling and visibility reductions. In most cases, such ambient impacts are localized in nature and not well documented and are dependent on combustion applicance density, meterological and topographical variations.

Visibility reduction is a more likely measurable impact of RWC emissions, because of the large percentage of fine particle emissions from these devices. It is estimated the mass median aerodynamic diameter is approximately 0.17 μm;

with particles less than 0.5 μm in diameter accounting for 83-90% of the total particle mass. Visibility reductions in urban and rural air sheds are due primarily to the fine particles, with aerodynamic diameters of 0.1 to 1.0 μm.

Although, specific studies on visibility reductions due to RWC are not availabe, visibility impacts have been noted in some studies. Visibility reductions during specific time periods may be substantial, especially during nightime because of limited atmospheric dispersion, increases in charges of wood and the reduction of draft resulting in increased particle concentrations.

DISCUSSION

In general, environmental and health concerns regarding residential heating emissions have focussed on residential wood combustion. With the resurgence of wood as a residential fuel since the mid 1970's in North America, a number of ambient air and source apportionment studies associated with residential wood combustion have been conducted to measure the impacts of particulate matter (and particle size) and trace organics, specifically PAHs and in particular BaP on air quality.

Although a direct causal link cannot be established with respect to health and RWC emissions, there is enough evidence to suggest that high levels of emissions, especially of particulates could aggravate health problems among certain portions of the population. Also, enough is known about the properties of certain pollutants emitted from RWC activities to warrant action, in addition to nuisance effects reported in many localities. One unknown factor which is beyond the scope of the report was the indoor levels associated with the various residential combustion heating systems; and further research is suggested to determine the total human exposure to trace organics and particualte matter from this source.

In Canada, potential and actual environmental problems caused by RWC are very site specific and are related to population size, appliance density, climatic and topographical variations. Potential problem areas in Canada seem to be certain areas in the Yukon Territory, British Columbia, and certain localities in Atlantic Canada, Quebec and Ontario.

With the exception of the Whitehorse Yukon case, provincial and municipal authorities have approached the woodsmoke issue on a case by case basis. In some areas, monitoring of indoor and outdoor air is required to further delineate the extent of RWC health impacts.

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TABLE 1

Regional Trends in Residential Fuel Use in Canada, 1973, 1981 and 1986

Province/Territory	Principal Heating Fuels (% of households)[a]											
	Piped or bottled gas			Oil or kerosene			Electricity			Other (wood, coal)		
	1973 (1971)	1981	1986	1973 (1971)	1981	1986	1973 (1971)	1981	1986	1973 (1971)	1981	1986
British Columbia	46	58	54	44	22	16	8	18	21	3	3	8
Alberta	91	97	93	6	2	2	--	--	2	2	—	1
Yukon Territory	(2)	2		(79)	64		(3)	17		(17)	8	
Northwest Territories	(5)	4		(80)	82		(1)	6		(14)	8	
Saskatchewan	70	78	81	28	17	11	--	--	5	--	--	2
Manitoba	61	62	61	27	15	8	9	21	27	1	2	3
Ontario	40	52	60	52	32	18	7	14	19	1	2	3
Quebec	7	7	11	79	49	25	10	41	58	3	2	6
New Brunswick	--	--	2	90	63	36	4	24	40	6	12	22
Nova Scotia	—	—	2	88	79	64	3	9	15	9	11	19
Prince Edward Island	—	--	--	93	80	69	--	--	--	--	14	26
Newfoundland	--	--	--	85	53	34	9	35	37	5	13	29
Canada	35	42	46	56	34	20	7	21	28	3	3	6

[a]The term "households" refers to occupied private dwellings, including single and semi-detached houses, duplexes, row houses, apartments, condominiums and mobile homes.

TABLE 2

A Comparison of Emission Factors for Oil and Gas-Fired Furnaces and Wood Stoves

Compound	Emissions		
	Oil Furnaces[a]	Gas Furnaces[b]	Wood Stoves
	$ug.J^{-1}$[c]	$ug.J^{-1}$[d]	$ug.J^{1-1}$
NO_x	0.057	1.2×10^{-3}	0.07
CO	0.016	2.4×10^{-4}	6.5
Particulates	0.008	6.1×10^{-5}	1.05
SO_2	0.308[e]	7.3×10^{-6}	0.01
VOC[f]	0.02	6.4×10^{-5}	2.55
POM	2.5×10^{-4}	4.5×10^{-7}	9.5×10^{-3} 18.5×10^{-3}

a Heat rate 0.5×10^9 J/hr.
b Heat input 10^6 Btu/hr.
c Based on 38.6 KJ/L of fuel oil.
d Based on 1313.9 MJ/m^3 of natural gas.
e Assuming sulphur content of 0.7%.
f Volatile organic compounds (excluding methane).

Nationwide Emissions of Air Contaminants (1980)
(in 1000s of tonnes)

Category	Particulate Matter	% of Total	Sulphur Oxides[a]	% of Total	Nitrogen Oxides[b]	% of Total	Hydrocarbons	% of Total	Carbon Monoxide	% of Total
Industrial Processes	1 216	63.8	3 127	67.2	48	2.8	572	30.6	609	5.9
Fuel Combustion/ Stationary Sources (Non-Residential)	217	11.4	1 314	28.3	532	30.8	58	3.1	68	0.7
Residential Fuel Combustion (Excluding Fuelwood)	6	0.3	67	1.4	45	2.6	6	0.3	20	0.2
Fuelwood Combustion	88	4.6	3	0.1	5	0.3	3	0.2	393	3.8
Transportation	98	5.2	137	2.9	1 072	62.2	797	42.6	7 776	75.6
Solid Waste Incineration	33	1.7	3	0.1	5	0.3	31	1.7	374	3.6
Miscellaneous	248	13.0	--	--	18	1.0	403	21.5	1 053	10.2
TOTAL	1 906	100.0	4 651	100.0	1 725	100.0	1 870	100.0	10 293	100.0

a expressed as SO_2

b expressed as NO_2

TABLE 4

Emissions from Residential Fuel Combustion in Canada, 1985
(tonnes)

Fuel Type	Particulate Matter	SO_2	NO_x	CO	HC	VOC*	PAH*
Natural Gas	640	130	21 330	4 270	1 710	1 120	8
Light Oil	1 460	22 150	10 740	2 930	1 560	420	46
Heavy Oil	280	3 650	630	60	20	10	N.A.
Kerosene and Stove Oil	170	1 030	1 220	330	170	50	N.A.
LPG	380	150	1 280	260	110	70	N.A.
Coal	1 360	2 790	270	8 170	1 630	910	11
SUB-TOTAL	4 290	29 900	35 470	16 020	5 200	2 580	65
Fuelwood	151 660	3 650	4 530	607 000	105 100	104 290	175
TOTAL	155 950	33 500	40 000	623 020	110 300	106 870	240

* Estimates based on consultants' studies.

RÔLES COMPLÉMENTAIRES DE LA BIOTECHNOLOGIE ET DE L'ÉCOTOXICOLOGIE POUR L'ÉTUDE DES CONTAMINANTS DANS L'ENVIRONNEMENT

COMPLEMENTARY ROLES OF BIOTECHNOLOGY AND ECOTOXICOLOGY FOR THE STUDY OF ENVIRONMENTAL CONTAMINANTS

Bernard Coupal*, Charles Greer*

* Institut de recherche en biotechnologie, Conseil National de Recherches du Canada, 6100, avenue Royalmount, Montréal, H4P 2R2, Québec, Canada.

et/and

R. van Coillie**

** Environnement Canada, Direction de la Protection de l'environnement, Région du Québec, 1179, rue Bleury, Montréal, H3B 3H9, Québec, Canada.

INTRODUCTION

Dans les préoccupations grandissantes de la protection de l'environnement, la gestion des contaminants toxiques constitue une priorité omniprésente. En amont de celle-ci, on vise à contrôler l'utilisation des produits toxiques. En aval, on est confronté avec les rejets, cheminements et/ou récupérations de ces composés dans l'environnement. Lorsqu'il n'est pas trop tard (ce qui s'avère le cas par exemple pour le DDT et Hg), la décontamination environnementale fait appel non seulement à des procédés physico-chimiques tels que la floculation et l'incinération mais aussi à des traitabilités microbiologiques. Parmi ces dernières, la biodégradation des contaminants toxiques offre un avenir prometteur grâce aux actuels progrès fulgurants de la biotechnologie surtout si on y couple l'écotoxicologie.

A cette fin, ces deux domaines interdisciplinaires en vogue se révèlent en effet très utiles et complémentaires, comme notre exposé désire l'expliciter. Il est focalisé vers deux groupes toxiques de haute priorité actuelle, à savoir les HAP (Hydrocarbures Aromatiques Polycycliques) et les BPC (Bi-Phényl poly-Chlorés). Il précisera d'abord le catabolisme de ces composés et ses débouchés biotechnologiques et montrera ensuite les apports des outils écotoxicologiques pour le suivi de leur détoxification.

MICROBIAL DEGRADATION OF ORGANIC POLLUTANTS

The ability of an organism to degrade an organic compound is dependent on several related factors, that can be summarized as follows;

1) The compound must be recognized as a substrate and mobilized or transported into the cell. Substrate mobilization could involve solubilization of the compound via surfactant production, and translocation inside the cell could be by passive diffusion, or by an active mechanism utilizing permeases.
2) The organism must possess the necessary enzymatic machinery to catalyze the degradation of the compound.
3) The compound must have the ability to act as an inducer for the synthesis of the enzymes required for its degradation.

Many aromatic and substituted (CH_3, Cl) aromatic compounds are only slightly soluble or insoluble in aqueous systems, whereas their solubility in lipid material may facilitate their uptake by passibe diffusion. In some instances however, specific transport systems do play a role in the uptake of these compounds (1). In certain cases, an organism will not completely degrade a compound, but will perform a specific enzymatic transformation in the presence of another growth substrate. This process of co-metabolism or co-oxidation (the enzymatic transformation of a compound where the organism does not derive any growth requirements from the reaction) is a common route for the detoxification of environmental pollutants (2).

BIODEGRADATION OF THE AROMATIC NUCLEUS

A large number of microorganisms, both procaryotic and eucaryotic, are capable of cleaving the aromatic ring (3). The initial reaction in preparation for ring cleavage in eucaryotes is the introduction of atomic oxygen, catalyzed by monooxygenases, generating arene epoxides which are then hydrated to yield trans-dihydrodiols. In contrast, procaryotes introduce molecular oxygen, catalyzed by dioxygenases, generating arene dioxetanes, which are subsequently reduced to give cis-dihydrodiols (4). Both dihydrodiols are subsequently re-aromatized to the corresponding diols. This fundamentally different activation process may have implications in the mutagenicity of many aromatic compounds in eucaryotes.

The prerequisite for fission of the aromatic ring is the presence of two hydroxyl groups located either ortho or para to each other (5). The scheme shown in Figure 1 is a generalized representation of the catabolic routes employed by different bacteria to initiate degradation of aromatic compounds. Toluene (12, Fig. 1), biphenyl (2, Fig. 1), naphthalene (23, Fig. 1) and phenanthrene (14, Fig. 1) are metabolized by bacteria using peripheral pathways that converge on catechol (9, Fig. 1). Catechol is subsequently degraded by either the ortho-pathway, yeilding cis,cis- muconic acid (10, Fig. 1), or by the meta-pathway, yeilding 2-hydroxymuconic acid semialdehyde (11, Fig. 1), with CO_2 as the ultimate end product of both pathways. Although the routes depicted here converge on catechol, different bacteria employ other mechanisms to funnel intermediates from aromatic degradation routes into central metabolic routes (Krebs cycle). For example, in the degradation of phenanthrene, 1-hydroxy-2-naphthoate (20, Fig. 1) can be degraded via the naphthalene pathway as shown, or through another peripheral pathway that generates a different series of intermediates.

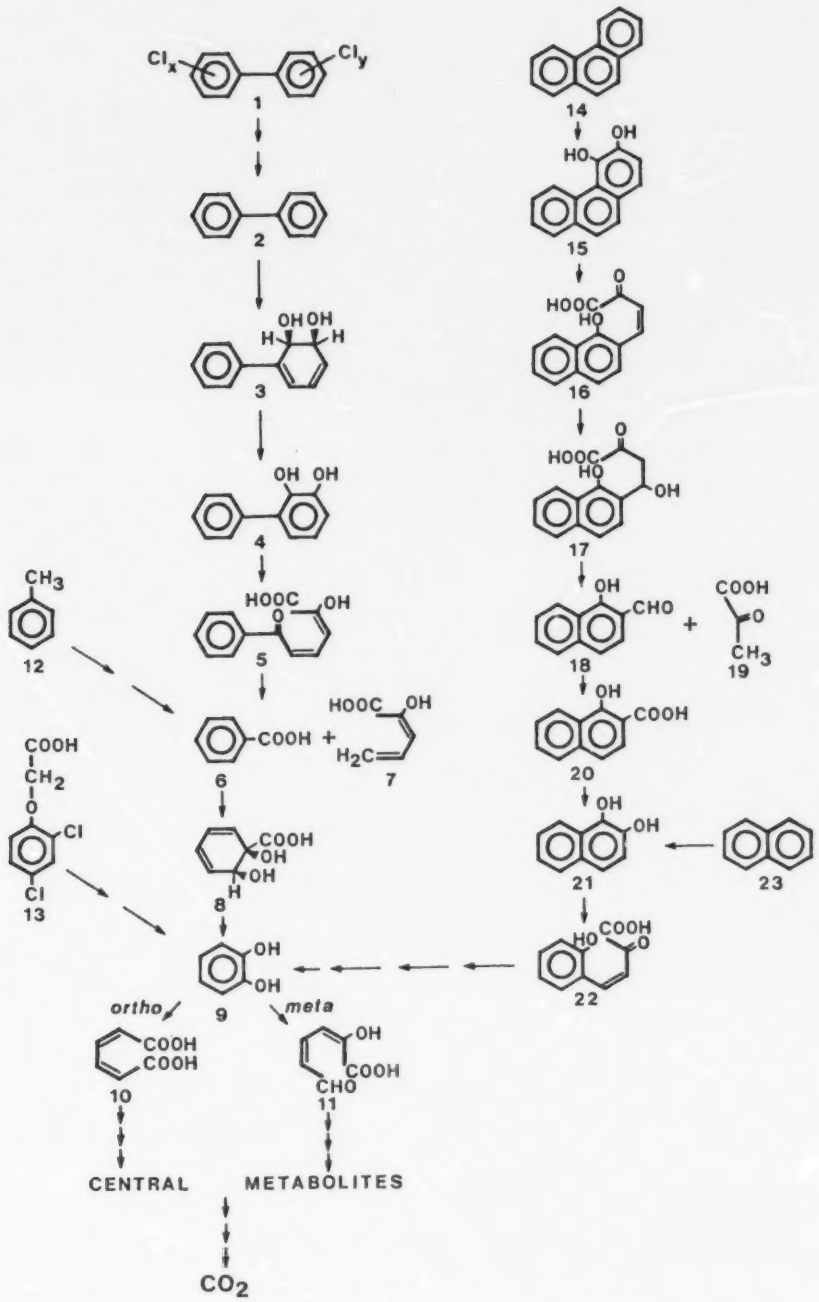
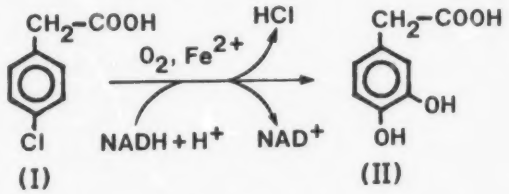


Figure 1. Generalized scheme for the catabolic routes of representative aromatic compounds employed by different bacteria. (2=biphenyl, 12=toluene, 14=phenanthrene, 23=naphthalene).

BIODEGRADATION OF CHLORINATED AROMATICS

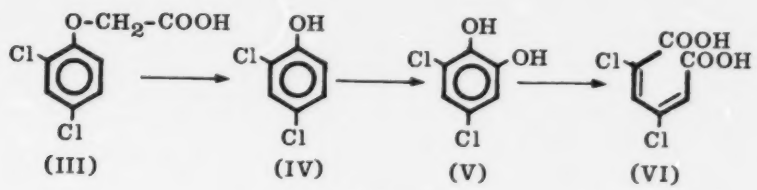
Chlorinated organic compounds are not exclusively man-made (xenobiotic), many are of natural origin. In fact, over 200 naturally occurring halogenated organic compounds have been identified (6). As a result, microorganisms have had the opportunity to evolve degradative functions to deal with some chlorinated compounds, although microbial exposure to many xenobiotics is a more recent phenomenon. Substitution of the aromatic nucleus with chlorine tends to increase both the toxicity and recalcitrance of a compound. The recalcitrance of chloroaromatics is inherently related to the properties of these compounds as heat-transfer fluids, lubricants, insulators, insecticides and herbicides. Despite the stability of chloroaromatics, many microorganisms have developed the ability to completely degrade these compounds to CO_2. Other microorganisms only partially degrade chloroaromatics, leading to the production of toxic or dead-end metabolites (1). A number of articles are available that deal with the microbial degradation of chloroaromatics in detail, and the possible uses of the microorganisms for the treatment of pollution problems (1,7-12).

To degrade a chloroaromatic, a microorganism must recognize the compound as a substrate, mobilize it, and possess the necessary regulatory and enzymatic functions responsible for its degradation. Chloroaromatic compounds are degraded by bacteria using two basic mechanisms. In the first, the chlorine is specifically removed, as an initial step, followed by the degradation of the aromatic nucleus. In the second mechanism, the chloroaromatic is degraded by aromatic pathway enzymes that accept substituted substrates. Anaerobic bacteria, which are representative of the first mechanism, have been shown to degrade chlorobenzoic acids by reductive dechlorination yielding benzoic acid (6, Fig. 1) as an intermediate (13). The subsequent degradation of benzoic acid by anaerobic bacteria involves saturation of the ring to give cyclohexane carboxylic acid, followed by a ring cleavage pathway that yields aliphatic acid substrates (14). Similarly, anaerobic bacteria are known to participate in the reductive dechlorination of polychlorinated biphenyls, PCB's (1, Fig. 1) (15). In the second mechanism for the degradation of chloroaromatics, an aerobic bacterium has been shown to replace chlorine on the ring, catalyzed by an enzymatic complex incorporating a reductase and an oxygenase function (16, 17). The 4-chlorophenylacetate substrate (I, Scheme 1) was dechlorinated and dihydroxylated to yield an acetate substituted catechol (II, Scheme 1), which was then degraded by a meta-cleavage pathway (see 9-11, Fig. 1).



Scheme 1

In other aerobic bacteria, as seen for the degradation of some herbicides and PCB's, the chloroaromatics are metabolized by pathways that incorporate broad substrate specificity enzymes that can catalyze reactions with both chlorinated and non-chlorinated substrates. As an example, chlorobenzoic acids are degraded by Pseudomonas sp. (18) using the same pathway as for benzoic acid (6, Fig. 1). The herbicide 2,4-dichlorophenoxyacetic acid, 2,4-D, (13, Fig. 1; III, Scheme 2) is degradedd by an Arthrobacter sp. using a modified version of the ortho-pathway (19), known as the chlorocatechol pathway. The first intermediate is 2,4-dichlorophenol (IV, Scheme 2), which is converted to 3,5-dichlorocatechol (V, Scheme 2), and cleaved to yield 2, 4-dichloromuconic acid (VI, Scheme 2). The chlorines are lost non-specifically during the subsequent degradation to yield the central metabolite, succinic acid.



Scheme 2

Microbial degradation of the defoliant 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) occurs by a similar process (20).

Aerobic bacteria have been shown to degrade PCB's using broad substrate specificity enzymes of the biphenyl pathway (1-2, Fig. 1). The number of possible PCB congeners (209 max.), and the variety of congeners typically present in commercial products (often in excess of 50) (21), limits the extent to which individual microorganisms can degrade them. A number of general observations have been made concerning the degradation of PCB's by microorganisms (22);

a) Degradation decreased as chlorine substitution increased

b) PCB's containing two chlorines in the ortho position of a single ring (2,6-), or both rings (2,2'-) showed poor degradability

c) PCB's containing all chlorines on one ring only were metabolized faster than PCB's having the same number of chlorines substituted on both rings.

ROLES OF BIOTECHNOLOGY IN BIODEGRADATION OF ORGANIC POLLUTANTS

Many of the degradative pathways employed by microorganisms to degrade aromatic compounds are plasmid encoded (11). Plamids such as the TOL and NAH plasmids, contain all the genes necessary to code for the enzymes required for the degradation of their respective substrates, toluene and naphthalene. A number of these plasmids have been extensively characterized, and in some cases, new plasmids have been developed that impart increased degradative functions to the recipient (8, 11, 23). Using the techniques being developed to manipulate degradative functions, microorganisms can now degrade chloroaromatic compounds that they could not

previously degrade. In addition, some microorganisms that could partially degrade compounds leading to the production of toxic or dead-end metabolites, can be manipulated to enable them to complete the degradation. In instances where the use of whole microbes is not feasible, enzymatic procedures can be utilized. For example, the destruction of PCB's once they have entered the environment is a difficult problem. Use of either bacteria able to dechlorinate PCB's, or the dehalogenting enzymes alone, would greatly accelerate their disappearance, since many soil and aquatic bacteria possess the ability to utilize biphenyl as a source of carbon.

Biotechnology is already an important factor in the development of reliable, economic procedures to treat environmental pollutants. Efforts are being directed at selecting microorganims with improved degradative functions, and adapting them to enhance their abilities to deal with toxic chemicals. In addition, the genetic manipulation of existing strains, to increase and diversify their degradative functions, will achieve similar objectives. The development of any large-scale treatment process to deal with environmental pollutants will require the efforts of both microbiologists and engineers, as considerable obstacles must be overcome before this objective can be realized.

COMPLÉMENTARITÉS ENTRE BIOTECHNOLOGIE ET ÉCOTOXICOLOGIE

Tandis que la biotechnologie utilise des organismes biologiques pour produire des biens et/ou services comme la biodégradation des contaminants toxiques dans le présent cas, l'écotoxicologie emploie des organismes biologiques pour évaluer avec des bioessais et/ou des bioindicateurs divers changements environnementaux commes les effets des produits toxiques et de leurs dérivés. A première vue, différents, des deux domaines sont cependant appelés à oeuvrer ensemble... malgré un manque de communication entre leurs spécialistes (24).

De fait, d'une part, la biotechnologie peut fournir les apports suivants à l'écotoxicologie:

(i) déceler la présence de toxicités chimiques, bactériologiques ou virales particulières à l'aide de biocapteurs, microorganismes ou anticorps monoclonaux spécifiquement sensibles: il est notamment connu que des petites concentrations de NH_3, Salmonella proteus ou virus grippal sont ainsi facilement détectable;

(ii) améliorer le coût/bénéfice de certains microbioessais écotoxiques en proposant des microorganismes génétiquement optimisés à des fins écotoxicologiques: par exemple, la bioluminescence étant rapidement inhibée (5 minutes) par une large gamme de composés toxiques et d'effluents chez Photobacterium phosphoreum (25), elle a fait l'objet d'une transfert de ses gènes chez Escherichia coli pour un dépistage accru des écotoxicités (26);

(iii) recommander plusieurs microorganismes pour tester la biodégradabilité de la toxicité de rejets complexes: entre autres, les bactéries Pseudomonas sp., Flavobacterium sp., Arthrobacter sp. ou Mycobacterium sp. et les champignons Candida sp., Clodosporium sp., Trichosporium sp. ou Rhodotorula sp. ont une capacité de biodégrader les hydrocarbures pétroliers (27).

Par ailleurs, d'autre part, l'écotoxicologie peut aider la biotechnologie avec les contributions stipulées ci-après:

(iv) préciser la toxicité des microorganismes ou des produits biotechnologiques: par exemple, la firme Monsanto a déterminé les effets écotoxiques de différents pesticides biologiques envers des cibles non visées telles que les puces d'eau Daphnia magna (24);

(v) estimer les impacts d'une introduction accidentelle ou intentionnelle de microorganismes et/ou de produits biotechnologiques dans un environnement particulier; des microcosomes aquatiques ou pédologiques sont mis au point à cette fin;

(vi) proposer des méthodologies d'évaluation de risque en tenant compte de diverses variables (écoulement, lessivage, transport sédimentaire, saisons, etc.) pour les retombées biotechnologiques dans l'environnement.

L'intérêt des biotechnologistes et des écotoxicologistes à oeuvrer ensemble se vérifie notamment pour la biodégradation des polluants organiques, entre autres les HAP et les BPC, comme l'indiquera la suite de l'exposé.

RÔLES DE L'ÉCOTOXICOLOGIE DANS LA BIODÉGRADATION DES POLLUANTS ORGANIQUES

Les grandes tendances de l'écotoxicologie se résument comme suit:

- relations quantitatives entre la structure et l'activité d'un produit toxique (QSAR) (28);
- persistance, cheminement, bioaccumulation et/ou biotranformation des composés toxiques (29);
- dépistage et ensuite détermination des écotoxicités possibles au moyen de bioessais létaux, sous-létaux et chroniques (30);
- évaluation des risques (31).

Compte tenu de ces tendances, quelles sont les implications de l'écotoxicologie pour la dégradation biotechnologique des toxiques organiques? Ces implications, orientées principalement vers la toxicologie aquatique vu que le milieu aquatique représente le terminus plus ou moins direct du cheminement des contaminants environnementaux (29), visent à aider à focaliser la biodégradation de ces toxiques, comme l'illustrent les trois questions énoncées ci-dessous.

I. Quelles sont les formes les plus toxiques qui doivent recevoir une attention prioritaire pour leur biodégradation lorsqu'on est en présence d'un toxique complexe? Pour répondre à une telle question, mentionnons par exemple que des bioessais permettent de préciser des ordres décroissants d'écotoxicité pour les BPC suivants (32):

- 3, 4, 5, 3', 4', 5' > 2, 4, 6, 2', 4', 6' > 2, 4, 5, 2', 4', 5' > 2, 3, 4, 2', 3', 4' (létalité du talitre Gammarus pseudolimnaeus exposé à des isomères hexachlorobiphényles);

- Aroclors 1248 > 1254 > 1260 > 1262 > 1242 > 1232 >1221 > 1268 (létalité du zooplancton Daphnia magna exposé à des mélanges commerciaux).

II. Lors de la biodégradation d'un toxique complexe, comment évolue son écotoxicité? A ce sujet, signalons que des bioessais faits avec des bactéries estuariennes indiquent que la biodégradation des HAP peut laisser une écotoxicité résiduelle due au benzo-a-pyrène (33). Ajoutons qu'une biodégradation des HAP menant à des naphtols et des phénols (tels que la catéchol) se révèle insuffisante car ces dérivés excercent encore une toxicité importante (27).

III. Une mutagénicité peut-elle se manifester dans un toxique complexe lors de sa biodégradation? Des biotests d'Ames avec Salmonella typhimurium détectent effectivement une mutagénicité dans du pétrole en cours de biodégradation, le benzo-a-pyrène mutagène n'étant plus alors masqué par un grand nombre de composés non mutagènes (27). La bonne corrélation entre les propriétés mutagènes et le pouvoir cancérogène de divers contaminants (34) donne une importance indéniable à ce type d'information. Notons d'ailleurs à ce propos que l'activation métabolique des HAP rend certains de ceux-ci cancérogènes et mutagènes, ce qui peut affecter la biodégradation (27).

Bref, les bioessais proposés par l'écotoxicologie (leur énumération serait trop longue ici) permettent un suivi et un contrôle de la détoxification lors des dégradations biotechnologiques des polluants organiques.

CONCLUSION

La plupart des contaminants toxiques environnementaux (excepté les métaux lourds) peuvent être biodégradés par cométabolisme dans des microorganismes bactériens ou fungiques. Ceci se vérifie notamment pour les BPC (Bi-Ph ényles poly-Chlorés) et les HAP (Hydrocarbures Aromatiques Polycycliques) via des déchlorinations, oxygénations, hydroxylations, fissions aromatiques et/ou décarboxylations qui mènent au succinate du métabolisme.

La biotechnologie exploite et accélère cette dégradation microbiologique en optimisant ses conditions: substrat enrichi, souches bactériennes améliorées par génie génétique, apport enzymatique sélectif, etc.

L'écotoxicologie aide à focaliser la dégradation biotechnologique des contaminants toxiques, entre autres les BPC et HAP, en explicitant les cibles prioritaires à traiter et en offrant un suivi et/ou contrôle de la détoxification au moyen de différents bioessais (létaux, sous-létaux, génotoxiques et/ou bioaccumulatifs).

Les succès de la décontamination toxique environnementale dépend à l'avenir de telles interdépendances entre biotechnologie et écotoxicologie.

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REMERCIEMENTS

Les auteurs expriment leur vive gratitude à Mme Jocelyne Brais pour la dactylographie de leur texte.

STRATÉGIE DE GESTION DES SOLS CONTAMINÉS : PERSPECTIVE INTERNATIONALE

M. Beaulieu, S. Goulet, S. St-Laurent
Direction des substances dangereuses
Ministère de l'Environnement du Québec

INTRODUCTION

La prise de conscience au niveau mondial de problèmes posés par l'existence de sols contaminés est très récente. Après les avertissements servis par les cas de Lekkerkerk (Pays-Bas), Love Canal (Etats-Unis) et tout récemment le cas de Ville LaSalle au Québec, il a fallu quelques années pour que l'on réalise qu'il ne s'agissait que de la pointe de l'iceberg; plusieurs décennies de mauvaise gestion au niveau de l'élimination des déchets industriels toxiques ont marqué à leur façon l'environnement.

Ainsi, différents outils ont été développés pour gérer adéquatement les déchets dangereux. Cependant, toutes les données devenaient insuffisantes ou inadéquates lorsque venait le temps de gérer les sols. En fait, les sols contaminés peuvent difficilement être considérés comme des déchets dangereux. On entend par déchet dangereux toute substance (corrosive, inflammable, lixiviable, radioactive, réactive ou toxique) générée par les différents procédés industriels.

On s'est cependant rendu compte que le problème des sols contaminés était de nature différente. Les sols contaminés sont des sols qui contiennent des concentrations non-naturelles de différents contaminants. Ces sols contaminés sont générés suite aux activités quotidiennes de commerces et d'industries suite à:

- des fuites de conduits ou de réservoirs;
- des déversements accidentels.

Même si ces sols diffèrent des déchets dangereux, il n'en demeure pas moins que la présence même faible de contaminants dans les sols peut, dans bien des cas, porter préjudice à la santé publique et à l'environnement.

Depuis une dizaine d'années, nous sommes témoins, en Amérique du Nord, de la fermeture et de la démolition d'un grand nombre d'entreprises vétustes. Ce phénomène, appelé à s'accélérer dans les années à venir, pose un problème préoccupant, celui du réemploi de terrains possiblement contaminés.

De fait, plusieurs entreprises, aujourd'hui fermées ou démolies, ont pu utiliser des substances dangereuses et ainsi contaminer le sol environnant par des rejets liés aux opérations journalières, par des déversements accidentels, ou par de l'élimination pure et simple sur leur terrain.

De plus en plus de promoteurs construisent des complexes résidentiels et commerciaux sur d'anciens terrains industriels, attirés par les faibles coûts de revient de ces terrains, souvent localisés près des centres-villes. Ces terrains sont également réutilisés, quoique plus rarement, à des fins récréatives, agricoles ou à d'autres fins industrielles.

Considérant les nouveaux usages envisagés pour ces terrains, il devient alors indispensable d'évaluer les impacts potentiels de la présence de contaminants dans les sols et l'eau souterraine sur la santé et la sécurité publique ainsi que sur l'environnement. La présence de contaminants dans les sols

peut également avoir des impacts au niveau de la structure des bâtiments:

- infiltration possible de contaminants dans le réseau d'aqueduc;
- dégradation possible des fondations en béton;
- accumulation possible de gaz de décomposition ou de contaminants volatils.

Tous ces risques potentiels pourront évidemment avoir des impacts économiques et sociaux importants:

- perte d'usage des sols;
- craintes pour la santé;
- perte de valeur de la propriété ainsi que de celles avoisinantes.

Considérant tous ces faits, il est indispensable, dans l'intérêt de tous les intervenants (promoteurs, municipalités, gouvernement, citoyens...) que les terrains soient caractérisés et, si nécessaire, restaurés de façon à en permettre la réutilisation. Depuis quelques années, de nombreux promoteurs, consultants ou citoyens se tournent vers les gouvernements afin d'obtenir de l'information. De nombreuses questions sont régulièrement posées:

- Doit-on permettre le redéveloppement sur des sols contaminés?
- Jusqu'où doit-on décontaminer les terrains avant de les réutiliser?

Pour faire face à ce nouveau problème, les divers gouvernements ont dû mettre au point différents outils de gestion dont:

- l'élaboration de critères d'évaluation de la qualité des sols et de l'eau souterraine;
- la mise en place de moyens pour gérer sécuritairement les sols contaminés, tels:
  - . l'enfouissement sécuritaire;
  - . les traitements thermiques, biologique et physico-chimique;
  - . le confinement sur place.

Cependant, même si les techniques de caractérisation et de restauration continuent d'évoluer, tous ces efforts de recherche et développement seront inutiles si les divers gouvernements ne disposent pas de programmes bien structurés leur permettant d'intervenir afin de s'assurer qu'il n'y ait plus de terrains contaminés qui soient utilisés pour la construction (industrielle, résidentielle ou commerciale) ou à des fins agricoles sans avoir fait l'objet des mesures de contrôle nécessaires.

Ces types d'interventions gouvernementales font intervenir une foule de dispositifs légaux qui varient selon les états. Le présent exposé présente une syntèse de trois approches utilisées pour régler le problème des sols contaminés. Nous présenterons les approches:

1) De la Hollande
2) Du New-Jersey
3) Du Québec

1. Approche des Pays-Bas

C'est en 1978 que la Hollande a été confrontée pour la première fois au problème des sols contaminés. Lekkerkerk, un petit village situé au nord de Rotterdam représente un des cas les plus spectaculaires jamais vu. Après que deux employés furent victimes d'étourdissements dans des tranchées lors de l'inspection de conduits de gaz, on découvrit qu'une partie des matériaux de remblai utilisés au moment de la construction étaient constitués de barils de produits chimiques et industriels. En 1980, les 800 résidants de 270 maisons durent être évacués pour une période de 6 à 9 mois. Au total, 86 700 m^3 de sol

contaminé a été excavé de sous ces maisons ce qui a représenté un coût total d'environ 100 millions de dollars. Puisque ces maisons étaient construites sur des pilotis, les sols contaminés ont pu être excavés et remplacés par du sol propre sans que les maisons ne soient démolies.

En 1983 le Gouvernement Hollandais a demandé aux provinces de dresser la liste des lieux contaminés afin de les caractériser et au besoin de les restaurer dans les années à venir. Trois facteurs sont pris en considération afin de déterminer si un lieu représente un risque sérieux pour la santé publique ou l'environnement:

- la nature et la concentration des différents contaminants présents dans les sols et l'eau souterraine;
- la facilité avec laquelle ces contaminants pourront migrer et ainsi affecter les personnes avoisinantes;
- les utilisations prévues du sol afin de bien évaluer les risques d'exposition des personnes aux différents contaminants.

Afin de faciliter l'interprétation des résultats d'analyses des sols et de l'eau souterraine, les Hollandais ont développé des critères (grille ABC) qui sont utilisés comme indicateurs du niveau de contamination:

A: la valeur A correspond au bruit de fond ou à la limite de détection de la méthode d'analyse;

B: lorsque les concentrations excèdent le critère B, la valeur du bruit de fond habituel est dépassée et une investigation supplémentaire est nécessaire.

C: lorsque les concentrations excèdent le critère C, habituellement des mesures correctrices doivent être prises.

Une liste de plus de 5000 lieux dont les sols sont contaminés a été dressée aux Pays-Bas. Tous ces efforts se sont soldés par l'adoption en 1983 d'une loi intérimaire dont on connaît la version anglaise sous le nom "Soil Clean-up (Interim) Act". Depuis 1987, il s'agit d'une loi définitive.

La philosophie de base en est fort simple. En ce qui concerne les sols, le gouvernement néerlandais a mis de l'avant le principe de la "conservation de l'usage multiple des sols". Il s'agit de garder, pour ces terrains, toutes les options ouvertes. Ce qui revient à décontaminer au maximum (en tenant compte des limites techniques et économiques) pour le futur. Les coûts élevés encourus pour la restauration des terrains sont une façon d'inciter les compagnies et la société à passer à l'étape de la prévention. Le Ministère est en train de passer d'une politique orientée sur les effets à une politique orientée sur les causes.

En pratique, les travaux de restauration sur les sols contaminés ont été effectués sur de "vieux cas" où le gouvernement devait défrayer les coûts. On tente maintenant d'impliquer de plus en plus les compagnies, mais celles-ci proposent leurs propres solutions (traitement sur place) et ne sont guère enthousiastes en ce qui a trait au principe de "l'usage multiple des sols".

Les grandes industries essaient:

- d'éviter que la contamination se trouvant sur leur terrain ne déborde à l'extérieur de leur propriété;
- de traiter sur place (ex.: compagnies pétrolières, land-farming sur un coin de leur terrain);
- d'aller vers des solutions à moindre coût.

Dans ce contexte, les industries remettent en question le principe "d'usages multiples" et contestent les critères de décontamination à appliquer aux

terrains industriels. Pour l'avenir, il devrait y avoir des normes par secteur d'activité en fonction de l'usage prévu des terrains.

La loi devenue effective le 1er janvier 1987 oblige maintenant tout promoteur à caractériser le sol et l'eau souterraine avant toute construction. A cet effet, un devis standard de caractérisation a été élaboré et celui-ci prévoit, pour un terrain de 1 acre, le prélèvement de 4 échantillons de sol ainsi que l'installation d'un piézomètre afin d'effectuer le prélèvement d'un échantillon d'eau souterraine. En Hollande, presque toutes les constructions sont subventionnées par l'Etat. L'obtention de la subvention dépend donc de la réalisation du programme d'échantillonnage et de la restauration des sols.

Notons que le budget annuel alloué par le gouvernement néerlandais pour le traitement des sols contaminés est de 100 millions de dollars par année. D'ici l'an 2000 on prévoit faire le nettoyage de plus de 2,5 millions de m^3 de sols contaminés.

Depuis janvier 1988, tous les terrains industriels sont maintenant visés par cette loi. Ainsi, avant de s'installer, la compagnie doit caractériser les sols et l'eau souterraine. Au moment où elle désire modifier ou vendre ses installations, la compagnie doit effectuer une nouvelle caractérisation afin de remettre le terrain dans le même état qu'il était au moment de son installation. Cette mesure incite les industries à prendre grand soin de leurs terrains en:

- vérifiant la présence de fuites au niveau des conduites ou réservoirs;
- nettoyant les sols dès qu'il y a un déversement accidentel;
- évitant toute mauvaise gestion de leurs produits chimiques ou déchets industriels.

2. Approche de New-Jersey

C'est en 1984 que le New-Jersey s'est doté d'une loi permettant d'intervenir auprès des industries susceptibles de contaminer les sols. Cette loi se nomme "The Environmental Cleanup Responsability Act" que l'on désigne habituellement par son acronyme ECRA. Avec l'entrée en vigueur de cette nouvelle loi, au moment de vendre ou de modifier leurs installations, les industries susceptibles d'avoir contaminé leurs sols doivent remplir un questionnaire permettant de déterminer s'ils sont assujettis au programme ECRA. Près de 23 000 compagnies sont visées par le programme ECRA.

Lorsqu'une industrie est assujettie au programme ECRA, elle doit caractériser son terrain au niveau des sols et de l'eau souterraine. Les résultats obtenus sont comparés à des critères préétablis et lorsqu'il y a présence de contaminants à des concentrations excédant le bruit de fond, il peut devenir nécessaire de procéder à des travaux correctifs.

C'est le bureau de l'ECRA qui s'occupe d'émettre les différents certificats aux compagnies selon que:

- le lieu considéré n'est pas soumis au programme;
- une caractérisation du lieu a été effectuée et l'absence de contamination permet d'autoriser la vente du terrain;
- après caractérisation du lieu, des mesures de restauration ont été prises afin de nettoyer le sol et l'eau souterraine et que le terrain est maintenant apte à être utilisé pour le nouveau projet.

C'est seulement après l'obtention de ce certificat de l'ECRA que le nouvel acheteur obtiendra son prêt de la part d'une institution financière et que la transaction sera permise.

Afin de donner encore plus de poids à cette loi, trois types de pénalité ont été prévus afin d'en faciliter l'application:

- des amendes pouvant aller jusqu'à 25 000$ par jour peuvent être imposées à quiconque fournit de fausses informations à l'ECRA;
- le département de l'Environnement du New-Jersey (NJEPD) peut annuler toute transaction si le vendeur refuse de caractériser ou restaurer le terrain;
- tout acheteur a la possibilité de faire annuler la transaction et d'exiger des dommages s'il est prouvé que l'ancien propriétaire n'a pas respecté la loi ECRA.

Il s'agit de la loi la plus mordante en son genre aux Etats-Unis et probablement au monde. Cette loi était cependant devenue nécessaire car le New-Jersey est un petit Etat très industrialisé. D'ailleurs, le New-Jersey est l'Etat où l'on compte le plus de cas SUPERFUND dont plusieurs parmi les dix (10) plus importants. Cette nouvelle loi est donc le moyen de s'assurer que les industries ne fermeront plus leurs portes en laissant derrière elles des terrains contaminés que l'Etat devra nettoyer aux frais des contribuables.

Une section spéciale du département de l'environnement du New-Jersey emploie plus d'une centaine de personnes à la réalisation du programme ECRA. Fait à signaler, le coût de ce programme est défrayé directement par les utilisateurs. Le montant à débourser pour l'obtention du certificat de l'ECRA est établi selon un certain pourcentage du coût total du projet de caractérisation et de restauration. Les montants ainsi recueillis permettent de défrayer les coûts du programme pour le gouvernement.

Au début, on prévoyait devoir étudier environ une centaine de cas par année mais il y en a eu environ 1 200 dès la première année, ce qui a occasionné un engorgement du système la première année: il semble que le mécanisme soit mieux intégré maintenant.

Enfin, il y a deux remarques que l'on peut faire à propos du programme du New-Jersey:

1° Les financiers et promoteurs craignaient que cette loi engorge le processus de transactions immobilières. Les faits semblent démontrer qu'il n'en est rien et que même, au contraire, une telle loi encourage les promoteurs à acheter d'anciens terrains industriels puisqu'ils sont maintenant protégés. De plus, les gens commencent à s'habituer au fait qu'une transaction qui nécessitait de 60 à 90 jours ne pourra être complétée avant 6 à 9 mois dorénavant.

2° Certains intervenants trouvent que les critères de décontamination sont beaucoup trop stricts et par conséquent difficilement atteignables à coût raisonnable.

3. Approche du Québec

En 1985, le Québec a dû, lui aussi, faire face à un problème majeur : le cas de Ville LaSalle où des habitations étaient construites sur des terrains contaminés. En plus du problème relié à la présence de déchets dangereux, le ministère de l'Environnement était alors confronté à un problème tout à fait nouveau : celui des sols contaminés.

Les premières démarches furent donc de se doter d'outils d'intervention et, à cet effet, le Québec fit l'inventaire des différentes approches utilisées

à travers le monde. Parmi les approches étudiées, celle de la Hollande apparaissait comme la plus intéressante car elle permettait l'évaluation du niveau de la contamination des sols et de l'eau souterraine à partir de critères préétablis.

La grille des critères ABC a alors été adaptée aux conditions particulières du Québec. L'utilisation des critères ABC a permis de juger du niveau de contamination des échantillons prélevés à Ville LaSalle et ainsi d'identifier les zones nécessitant une intervention.

Par la suite, les travaux de restauration furent alors réalisés.

Durant l'été 1986, 130 000 m^3 de sols contaminés furent excavés, huit maisons multifamiliales durent être démolies et le sol excavé fut remplacé par du sol propre. Durant l'été 1987, les sols contaminés ont été enfouis dans une cellule étanche sur les anciens terrains de la compagnie LaSalle Coke. Le coût prévu de l'opération a été estimé à près de neuf (9) millions de dollars.

Parallèlement à ceci, de nombreux autres cas de moindre importance d'anciens terrains industriels dont les sols étaient contaminés ont fait l'objet d'investigations de la part de nombreux promoteurs désireux de réutiliser ces terrains. Suite aux demandes des différents intervenants ainsi qu'au nombre toujours croissant de cas à étudier, il devenait indispensable de se doter de mécanismes d'intervention. À cet effet, le Québec devrait adopter au printemps 1988 une "Politique de réhabilitation des terrains contaminés". Au moment de la mise sous presse de ce texte, la politique n'étant pas rendue publique, nous ne mentionnerons ici que les grandes lignes directrices soient :

- de favoriser la réutilisation d'anciens terrains industriels dans la mesure où la qualité des sols est compatible avec les usages projetés;
- s'assurer que les terrains seront correctement caractérisés et restaurés par les promoteurs;
- s'assurer que les sols contaminés soient traités, éliminés, entreposés ou enfouis de façon sécuritaire.

CONCLUSION

Bien que le problème des sols contaminés soit relativement nouveau, déjà quelques états disposent de lois ou programmes leur permettant d'intervenir. Il est important de souligner que plusieurs autres gouvernements dont la Californie et la Grande-Bretagne disposent également de programmes d'intervention dans le domaine mais nous avons préféré nous attarder aux approches des Pays-Bas, du New-Jersey et du Québec parce que ces gouvernements ont été les premiers à être confrontés au problème des sols contaminés.

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MANAGEMENT OF A SUPERFUND SITE

By
George Pavlou, US Environmental Protection Agency

INTRODUCTION

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly known as Superfund, was enacted in 1980 in response to the need for a mechanism to respond to releases and/or the threat of releases of hazardous substances that endanger human health or the environment.

During the first five years of the program a $1.6 billion Hazardous Substance Response Trust Fund was established to cover costs for its implementation which included the funding of cleanups of abandoned and uncontrolled hazardous waste sites. The law also authorized enforcement and cost recovery actions against the party or parties responsible for the pollution.

The United States Environmental Protection Agency is responsible for implementing the program whose guidelines and procedures are spelled out in regulations known as the National Contingency Plan (NCP) (40 CFR, Part 300).

The structure of each EPA Region's Superfund Program varies slightly however, for the most part, each contain the following program elements:

- A Remedial Branch
- An Enforcement Branch
- A Removal Branch
- A Program Support Branch

Remedial Program

Activities taken under the Remedial Program involve long term investigatory activities which result in the design and construction of permanent remedies.

Due to the large number of sites, a ranking system was established that evaluates the hazards and risks associated with each. Sites meeting or exceeding a pre-established score are proposed to be included on the National Priorities List (NPL) which is a list of the nations most serious hazardous waste sites. Once placed on the NPL, the site receives funding necessary to complete a four stage process, leading to final site remediation.

The four stage process followed at each site includes:

- Remedial Investigation/Feasibility Study (RI/FS)
  - Evaluates the type and extent of contamination.
  - Evaluates the risk posed on human health and the environment.
  - Proposes remedies necessary to eliminate all identified risks.
- Record of Decision (ROD)
  - Presents the plan of action proposed to remedy hazards posed by the site and provides background on the decision.
- Remedial Design (RD)
  - Details the design and specification for conducting the cleanup.
- Remedial Action (RA)
  - The construction or implementation phase that follows the approval remedial design.

Removal Program

The removal program was established in order to provide a mechanism to respond to emergency situations including: hazardous material spills, air releases of hazardous substances, transportation incidents involving hazardous materials and threats posed by abandoned or uncontrolled hazardous waste sites including

those on the NPL.

Removal actions are short term actions aimed at stabilizing or removing hazardous materials that pose a threat to human health or the environment. Typical activities include securing a site by installing fencing, providing temporary and permanent sources of drinking water to residents effected by groundwater contamination, the removal of tanks or drums of hazardous substances or the removal of contaminated soil.

The New Superfund

The knowledge gained during the first five years of program implementation has helped us realize how much larger and more complex the hazardous waste problem is in the United States today.

In recognition of this, on October 17, 1986, the Superfund Amendments and Reauthorization Act (SARA) was enacted. The new Superfund reauthorizes the program for five years and increases the size of the fund to $9.0 billion. In addition, it strengthens and expands the cleanup program, focuses on the need for emergency preparedness and community right to know, and changes the tax structure financing the fund. A breakdown of the new fund financing mechanism is presented in Figure I.

FIGURE I

SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT
FUND FINANCING MECHANISMS

Funds	Source
$2.50 billion	Broad based tax on industry
$2.75 billion	New tax on crude oil
$1.40 billion	Tax on basic chemical feedstock
$1.25 billion	From general revenue
$500 million	New tax on motor fuel
$300 million	To be recovered from companies found to be responsible for the pollution at any given site
$300 million	From interest

A comparison of the major elements and goals of the Original Law to SARA follows:

ORIGINAL LAW	SARA
Removal Program	Removal Program
• Sets removal action time limit at 6 months and project ceiling at $1 million.	• Raises limits to 1 year and $2 million.
• Includes waiver to limits based upon three criteria	• Adds additional waiver criterion for consistency with long-term remedial action.
• No provision.	• Requires removals to contribute to the efficient performance of any long-term remedial action.
Remedial Program	Remedial Program
• No mandatory schedules or goals.	• Contains goals for preliminary assessments and site inspections and mandatory schedules for new RI/FS starts and new remedial action starts.
• Requires the development and use of criteria and methods for determining extent of remedy. Remedial actions must also be cost-effective and consistent with the National Contingency Plan (NCP).	• Requires remedies to: - Be protective of human health and the environment - Be cost-effective - Attain applicable Federal and State standards - Utilize permanent solutions and alternative technologies to the maximum extent practicable. • Treatment which reduces the volume, mobility and toxicity of the waste is preferred as well as permanent destruction.
• Provides for ATSDR to establish disease registry, health effects literature inventory, list of restricted areas and to provide health screening and medical care.	• Requires ATSDR (with EPA) to prepare list of hazardous substances, to prepare toxicological profiles, and to conduct health effects research and health assessments. A disease registry may also be established.

ORIGINAL LAW

Remedial Program

- Provides for State involvement in response actions through cooperative agreements and contracts.

SARA

Remedial Program

- Requires the establishment of formal State participation regulations providing for document review and comment and participation in every phase of the program.

ORIGINAL LAW	SARA
Enforcement Program	Enforcement Program
• No provision	• Authorizes citizen suits.
• No specific provisions in statute. Settlements authorized under Agency policy.	• Authorizes settlement agreements with PRPs and establishes procedures and tools for reaching settlements.
• No specific provisions in statute. Review of remedy decisions has been on the record.	• Establishes an administrative record upon which a response action will be based.
• Authorizes criminal penalties for failure to provide required notifications.	• Provides civil and increases criminal penalties for these activities.
• Prohibits the use of Fund money for remedial action at Federal facilities.	• Confirms CERCLA's applicability to Federal agencies and requires Federal agency compliance with CERCLA requirements. Also prohibits use of Fund money for remedial actions.
Community Relations	
• No specific provisions in statute. Community relations is authorized under Agency policy.	• Establishes public participation requirements and authorizes technical assistance grants.

ORIGINAL LAW

Research and Development and Training

- No specific provisions in statute.

Emergency Planning/Community Right-to-Know

- No specific provisions in statute. Emergency planning and preparedness activities are authorized by the NCP and Agency policy.

SARA

Research and Development and Training

- Establishes a comprehensive research, development and demonstration program for alternative technologies; training programs for hazardous substance response; and hazardous substance research.

Emergency Planning/Community Right-to-Know

- Establishes a State and local planning structure, emergency notification and reporting requirements for facilities.

THE CLOTHIER DRUM SITE

INTRODUCTION

While selecting a site to speak about during this presentation, I had a choice of over 67 National Priority List sites in the State of New York alone. The Clothier site was selected because it involved all aspects of the Superfund Program.

With the topic of this presentation being "The Management Of A Superfund Site", the Clothier site offered a unique challenge in that;

- It is a State lead remedial site with EPA providing oversight.
- It involved EPA's Site Investigation and Compliance Branch and Office of Regional Counsel during continual negotiations with Potentially Responsible Parties (PRP's) that eventually led to a partial cleanup.
- EPA's removal program provided RP oversight and conducted their own cleanup.

  and

- Under an Interagency Agreement, the U.S. Fish and Wildlife Service provided an extensive study of the flora and fauna of the wetlands surrounding the site.

Site History/Description

The Clothier site is located in the Town of Fulton, NY which is approximately 12 miles northwest of Syracuse. The site is located in a rural area consisting primarily of farmland with networks of interconnected wetlands. To the east, the site is bordered by Ox Creek, a tributary of the Oswego River.

Prior to 1974, the property was used for the disposal of drums of waste from the Pollution Abatement Services (PAS), located in Oswego, NY. At the time,

PAS was a permitted commercial industrial waste incinerator. Over the years of operation, the facility experienced periods of operational difficulty during which, drums of waste were disposed at a number of properties in the area with the Clothier site being one of them. When PAS ceased operation in 1976, over 2,200 drums of waste had been disposed of at the Clothier site. The drums contained a wide range of contaminants which included: volatile and semi-volatile organic compounds, acids, caustics, cyanides, PCB and metals.

EPA and NYSDEC Involvement

Prior to the enactment of the Comprehensive Environmental Response and Liability Act (CERCLA) of 1980, very little or no funding was available to address the clean up of such sites. In 1982 a mechanism to rank these sites was developed and the National Priorities List was established. At this time, the Clothier site is ranked 560 out of 951 sites in the country.

Remedial Activities

Remedial activities at the site began in 1985 and were funded under CERCLA. The establishment of a Cooperative Agreement between EPA and the NYSDEC allowed the NYSDEC (with funding from EPA) to assume the role of lead agency and conduct activities necessary to develop a Remedial Investigation and Feasibility Study (RI/FS) with oversight by EPA. During the initial stages of the remedial investigation, it was observed that the drums were in an advanced state of deterioration and required immediate attention. In December 1985, the NYSDEC requested that EPA utilize its Removal Program to remove the drums while remedial activities continued in an effort to determine the extent of on- and off-site contamination.

Although action was to be taken by PRP's and under EPA's Removal Program, the NYSDEC continued efforts in preparing a Remedial Investigation and Feasibility Study of the site. Prior to the PRP and EPA Removal Actions NYSDEC contractors installed 10 groundwater monitoring wells, staged and sampled drums, sampled on and off-site soils as well as surface water and sediments in the adjacent wetlands.

Based on the review of preliminary results and a study of the geology of the area, groundwater contamination did exist this contamination was limited to the upper aquifer. This aquifer is not used as a potable water source. In addition, a study of the aquifer indicated that it was connected to the Ox Creek wetlands. The results of initial soil sampling indicated gross soil contamination did exist however, the resampling of soil conducted after both PRP and EPA cleanups indicated that soil excavation and removal activities greatly reduced the threat posed by contaminated soil. Although surface water sampling showed very little impact from the site, contaminants were found in sediment samples.

U.S. Fish and Wildlife Services

An overall evaluation of the sampling results indicated that the off-site migration of contaminants should be a major focal point of additional studies. Discussions between EPA and NYSDEC resulted in the utilization of the U.S. Fish and Wildlife Service (USFWS) to assess the biological affects of contaminants on the Ox Creek ecosystem. This work was performed under an existing interagency agreement.

The study proposed by the USFWS included the investigation of water, soil, plants and animals inhabiting the Ox Creek and its tributaries. A breakdown of the sampling plan is outlined below:

I. VEGETATION

A. High Root on Tuber Bearing Vegetation

II. FISH

A. Predators, Pickerel, Pike, Bass, Bluegill
B. Bottom Dwellers - White Sucker, Carp, Bullhead

III. REPTILE

A. Snapping Turtle

IV. INVERTEBRATES

A. Crayfish
B. Clams (Alternate)

V. MAMMALS

A. Shrew
B. Mink or Weasel

The study was proposed to include seasonal sampling activities and is expected to be completed by the Summer of 1988.

Overall, the RI/FS is presently being re-evaluated to include updated groundwater and soil sampling results. A final RI/FS and Record of Decision should be issued by September 1988.

PRP and EPA Removal Actions

After an assessment of the site was conducted by EPA's Removal Staff, it was determined that site conditions met the criteria of the National Contingency

Plan for Removal Actions. An Action Memorandum which is an internal EPA Funding Request was prepared and funding was secured in March 1986. Since funding had been approved for removal activities, it was required by Law to Notice PRP's of the agency's planned activities and give them an opportunity to do the work themselves. Over 140 PRP's were identified and after 1 month all but a handful of PRP's signed and "Order of Consent" which committed them to provide for the cleanup of part of the site. Since a number of the PRP's decided not to participate in the settlement, EPA utilized an enforcement strategy called a "Carve Out." As part of this carve out the settling PRP's were responsible for the removal of visibly contaminated soil and all drums on-site that did not require incineration or treatment. Non-settling PRP's were then issued an order to provide for the cleanup of all remaining drums.

The settling PRP's contacted Chemical Waste Management Inc. to perform their portion of the cleanup. On June 2, 1986, mobilization of equipment and personnel was initiated and all work was completed on October 24, 1986. This segment of the cleanup resulted in the removal of approximately 1,960 drums and cost in excess of $1 million.

Since the non-settling PRP's refused to comply with a Unilateral Order issued for the cleanup of all remaining drums, EPA's Removal Staff mobilized their Emergency Response Cleanup Services contractor on October 25, 1986. Cleanup activities consisted of the excavation of approximately 80 buried drums, and the sampling, staging and securing of all drums remaining on-site. A major snowstorm prevented work from continuing beyond mid- November.

In April 1987, after receipt of compatibility data, EPA remobilized their ERCS (Emergency Response Cleanup Services) contractor and proceeded to consolidate existing drums by bulking all drums within the same compatibility groups. Although waste disposal analyses were available for some of the compatible groups, due to EPA policy, only facilities that are in compliance with applicable State and Federal regulations can be used for the disposal, incineration or treatment of waste generated at EPA Funded Removal or Remedial Actions. Due to the limited number of commercial disposal facilities that are in compliance, the coordination of disposal is often extremely difficult and often very expensive. This factor, compounded by strict procurement requirements resulted in a three month delay in the disposal of the non-PCB, flammable waste streams. During July 1987, approximately 260 drums of flammable liquids and solids were accepted for incineration by Thermalkem Inc. of Rock Hill, South Carolina.

To date, 26 drums of PCB waste, decon water and 60-90 yards of stockpiled contaminated soil and debris remain at the site. With several PCB incinerators recently coming into compliance, final removal activities are expected to take place this spring.

HAZARDOUS WASTE MANAGEMENT - THE ALBERTA MODEL

J.S. Richardson
Chem-Security Ltd.

BACKGROUND AND HISTORY

Industry and government in Alberta have achieved a success story in one of the most controversial of environmental issues. Few will argue that the technology and capability to handle hazardous waste has been around for decades. However, the ability to deal with this issue from a social and political perspective is not an easy task.

The history of special waste and the struggle to introduce the first fully integrated special waste treatment and disposal facility into Alberta, traces a period of seven years starting in 1979 when the Alberta Government called for a moratorium on the siting of any hazardous waste facilities until the issue was fully investigated. As a result of the Government's perseverance, Alberta is the first jurisdiction in North America to host a fully comprehensive special waste management system which has, as its centerpiece, an integrated special waste treatment centre or facility. The official opening of this facility took place in September 1987, although the plant has been operational in part since November 1986.

THE SPECIAL WASTE MANAGEMENT SYSTEM

The Special Waste Management System that has been developed is comprised of several major components to ensure the System is comprehensive, integrated and accessible to Albertans.

- A gathering or Collection System that is the initial interface between the overall System and the generator. The system includes two Transfer Stations servicing the larger communities of Calgary and Edmonton, Collection Centres planned for the medium-sized residential areas and a system of Mobile Collection Service units operating on 'milk runs' for the smaller residential and rural communities. These mobile collection centres will comprise a small mobile laboratory and transportation/storage container, complete with a small crane attached to the tractor so that the unit is totally self-contained.

  The Collection System is managed by Chem-Security Ltd. although individual facilities may be operated by municipalities, chemical distributors or other third parties.

  The Danish Collection System was used as a model for the development of the Alberta Collection System with variations that acknowledged the much larger collection service area and lower population density.

- A transportation network connects the Collection System to the Special Waste Treatment Centre, and co-ordinates with the Treatment Centre's scheduled operating program.

  The Transportation System is also managed by Chem-Security Ltd. who use owner/operator vehicles on exclusive contract to Chem-Security Ltd. for the haulage of special wastes.

  The drivers are trained by Chem-Security Ltd. and operate under Chem-Security Ltd. licences, insurance and permits using trailers and other equipment provided by Chem-Security Ltd. Individual generators however, are not precluded from providing their own transportation, but in that event, the transportation provided must comply with the prevailing standards regarding to equipment and Alberta Standards established by Chem-Security Ltd. and must comply with the shipping schedule as directed by Chem-Security Ltd.

- At the centre of the System is the Special Waste Treatment Centre (the Treatment Centre) located near Swan Hills approximately 200 km northwest of Edmonton, Alberta, at which the special wastes arrive having been channelled through the Collection and Transportation Systems. Once received by the plant, the special wastes are verified, prepared for treatment, processed and the residuals disposed of by landfill cell or deepwell injection.

THE TREATMENT CENTRE - DESIGN CAPACITY

Prior to designing any industrial facility, it is essential to identify the market, service or product demand and in the case of the Treatment Centre it was necessary to identify the types and quantities of special wastes likely to be received for treatment and disposal. An inventory of wastes was compiled for Alberta by Reid Crowther & Partners in the study 'Hazardous Wastes in Northern and Western Canada' in 1980 and suggested that approximately 100,000 tonnes of special wastes were generated by industry, commerce and the private sector.

This could not, of course, be used as a design basis for the Treatment Centre since, from experience in other countries, it has been found the volume of waste that is actually received by such a plant may be as little as 20% of the total that may be available.

This is the phenomenon whereby, upon the implementation of regulatories governing the proper treatment and disposal of industrial and special (hazardous) wastes at posted prices, industries immediately look for ways to reduce their costs in this area. In other words, industry looks to reducing the amount of wastes they generate, or for which off-site treatment and disposal is required.

Given that the design, must proceed without prior knowledge of the level of regulation or how they may be phased in, it was difficult to assess with any degree of accuracy the amount of available waste that the Treatment Centre will receive for treatment.

Should the Treatment Centre be designed for a processing capacity that ultimately is less than the market, or volume of wastes requiring processing,

it is a fairly simple task to increase capacity by either operating additional shifts or adding capacity without impacting unit operating costs and therefore service charges.

However, if less than the design volume of waste is received by a resultant under-utilized Treatment Centre, the impact is dramatic, for not only do unit operating costs, and therefore service charges, escalate but there is a further and compounding effect.

The need for a conservative approach towards the Treatment Centre design was therefore, paramount, and in the case of Alberta 20,000 tonnes per annum was used as the design base - 15,000 tonnes organic wastes and 5,000 tonnes per annum other wastes.

Chem-Security Ltd. then established its project team, which included a representative from the Corporation and began the development and design of the Treatment Centre.

THE TREATMENT CENTRE - DEVELOPMENT PHASE

As has been mentioned, a great deal of attention has been paid to the European technology and experience in deciding upon the Alberta Program and System.

Once a project director was chosen, he and key personnel from the project team representing the owners and the operators, spent several weeks reviewing European facilities, discussing their merits and also their disadvantages with the operating staff. Perhaps the most important question asked of existing operators was - 'what would you do differently?'

The team visited many facilities including the oldest operating plant-KOMMUNEKEMI in Denmark with over 18 years operating experience - and the then newest - EKOKEM in Finland - in an attempt to decide upon the selection of an operator to add to the Alberta Treatment Centre design team.

The CHEM CONTROL A/S group was chosen as consultants to the project, principally because of the similarity between the Albertan and Danish program and the many years of operating experience available through the staff of KOMMUNEKEMI. In addition, recognizing the emphasis on incineration as the preferred treatment for the majority of wastes, assistance was solicited from B.A.S.F., Ludwighaven, during the selection of the incinerator for the Treatment Centre.

Finally, confident that there was strong European representation on the project design team, Chemical Waste Management Inc., the largest special waste management company in North America, was added to provide access to their considerable knowledge in the area of landfill design, stabilization and experience of operating within the E.P.A. regulatory environment - very similar to that anticipated for Alberta.

This team of international experts was cemented by a local engineering consulting firm, Delta Projects who were then charged with producing the preliminary design for the Treatment Centre. The terms of reference given the project design team was to develop a Treatment Centre according to the criteria:

- The market or Volumes to be treated, on a steady state basis will be 20,000 tonnes per annum of which 15,000 tonnes will be incinerable waste,

developed in two phases - 1st Phase to be 10,000 tonnes/annum of incineration capacity.

- The Treatment Centre must receive all wastes and be able to treat them safely.
- The Treatment Centre must meet and be able to exceed all anticipated regulations.
- Build Small - one can always add, but cannot easily reduce capacity.
- Build Flexible - one should plan facilities in such a way that they may be easily modified/expanded, to accommodate additional or new waste streams.
- Build Modular - as in the auto industry, one should standardize as much as possible on facility components to ensure easy access for replacement or additional parts and, of course, design and engineering costs, should it be decided to expand the plant.
- Review Options - there are numerous and increasing technological advances in the field of waste treatment and one should monitor these developments constantly in order to take advantage of new and innovative techniques and equipment, i.e. - one must keep an open mind.

Other items for consideration in the development and the design of the Treatment Centre included consideration of traffic flow on-site, integration with the Transportation and Collection Systems, a 'what if' review of backup systems to ensure public safety and environmental protection. Finally, the team was directed to ensure that there was a blending of European and North American experience and expertise in the overall design.

What has resulted is what we believe to be an excellent design and facility, a benchmark for other facilities of its type incorporating some very innovative designs and equipment ideas.

THE TREATMENT CENTRE - MAJOR COMPONENTS

The Treatment Centre can be broken down into process and non-process (or infrastructure) components. The infrastructure components represent the major portion of the plant costs to date and comprise:

- Reception area including gate/guard house, truck scales;
- Laboratory and Administration building including analytical laboratory, data processing, offices, etc.;
- Operations and Maintenance Building housing personnel changing rooms, visitor centre/training centre, lunchroom and a comprehensive electrical, mechanical and electric maintenance complex;
- Waste Reception and Storage area incorporating waste sampling, container processing, (including shredding and decanting);
- Stormwater Retention ponds - all run-off from the operations area is collected for potential deepwell injection;
- Water Supply and Treatment System including a Storage Reservoir and fire water distribution network;
- Covered Secure Landfill cells;
- Injection Deepwell - for the disposal of compatible treated waste water from treatment processes, Sewage Treatment Plant, truckwash, storm water retention ponds, etc.;

° Truck-Wash facilities.

The Treatment Centre has been cast as 'comprehensive' to reflect the omnibus nature of the service or treatment capabilities it offers. The Treatment Centre has been designed to contain processes and plant/equipment that enable it to treat and dispose of the myriad of special wastes that are generated within the Albertan industrial, agricultural, commercial, institutional and private sectors. The Treatment Centre Site Plan, Figure 1, illustrates the layout of these facilities and the infrastructure supporting them.

THE TREATMENT CENTRE - TREATMENT PROCESSES

Alberta's economy has a solid petrochemical base which is reflected in the proportion of wastes already identified as being primarily organic in nature.

It was anticipated that organics will represent close to 75% of the waste received at the Treatment Centre or 15,000 tonnes per annum for which the appropriate treatment is high temperature incineration. Maintaining a conservative approach to developing the Treatment Centre it was decide to install approximately 10,000 tonnes per annum incineration capacity initially until the market matures and demand reaches that level forecast in design brief.

THE INCINERATOR

The Treatment Centre design brief therefore called for a 10,000 tonnes per annum or 17.5 million BTU/hour high temperature incineration capacity with the flexibility to increase that to 15,000 tonnes per annum or 24 million BTU/hour.

This posed an interesting problem for the project group because traditionally hazardous incineration has been accomplished by means of rotating kilns, sized to enable the kiln to accept 45-gallon drums - the most accessible, and therefore popular form of container for the collection and shipment of wastes.

It is also generally agreed that a kiln of approximately 2 metres internal diameter is required to safely incinerate 45-gallon drums - due to mechanical considerations - and kilns of such a size have usually a far greater capacity than required for the volume of wastes to be incinerated in the Treatment Centre.

The solution was found through an innovative variation of the rotating kiln design by the Swiss engineering company, Von Roll of Zurich who had developed a small incinerator to use a research tool towards evaluating the combustion characteristics of prospective clients' wastes. As has already been stated, most generators store and ship wastes in 45-gallon drums- wastes supplied for research test burns are similarly shipped and Von Roll therefore required a small BTU capacity incinerator capable of incinerating 45-gallon drums.

Von Roll's solution was to develop the 'rocking kiln system', a compact

OVERALL SITE PLAN

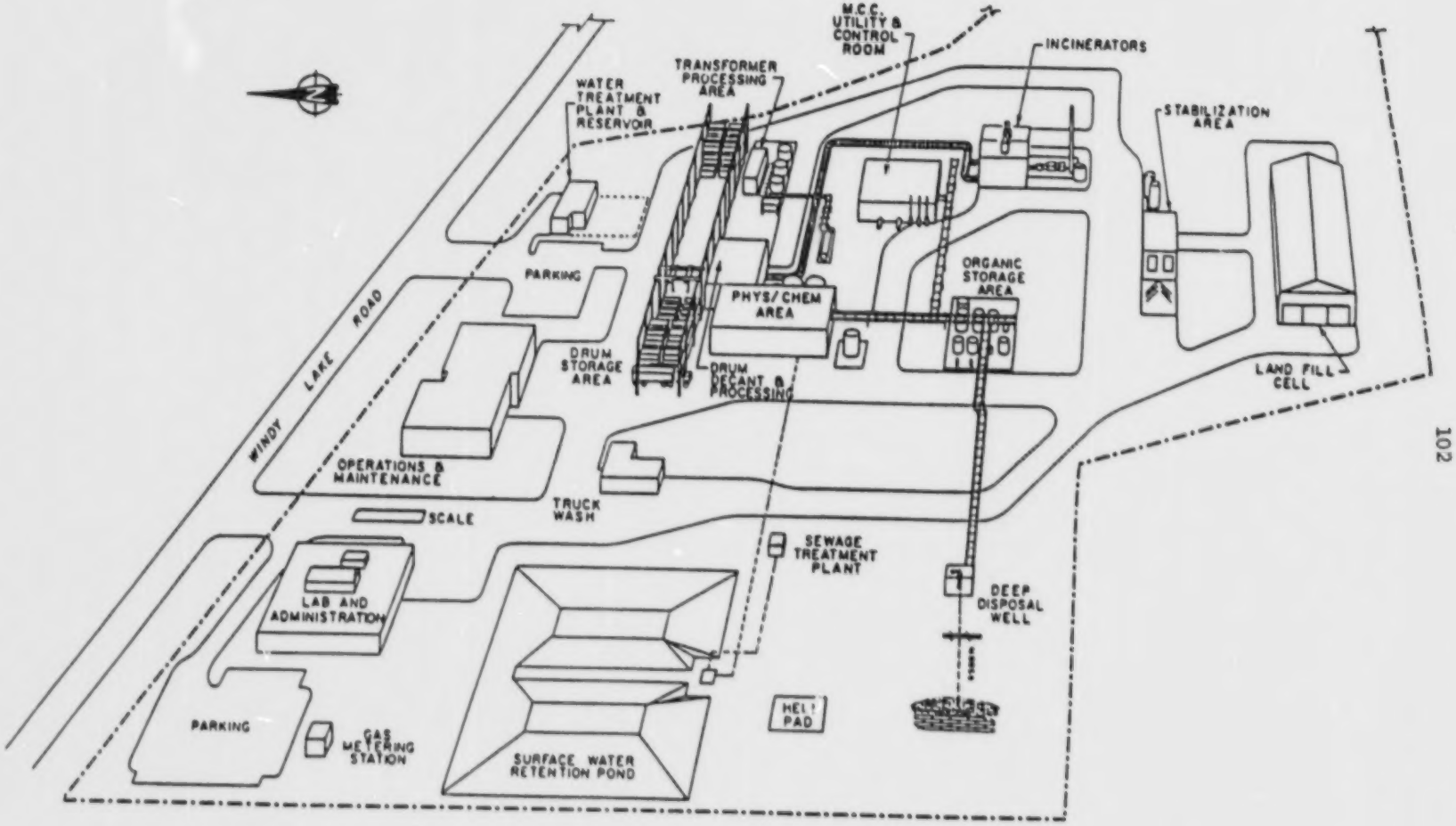


Figure 1

version of the rotating kiln that agitates or stokes the waste in the primary combustion chamber by a rocking rather than rotating motion.

The operating characteristics of the 'rocking kiln system' are identical to those of its rotating cousin, except in its 'batch' discharge of residuals - all other systems, secondary combustion chamber, loading, fuel, air pollution control train, stack, etc., are essentially the same.

The key element of the system is the rocking kiln furnace designed to be capable of controlled incineration of wastes in containers or drums without any pre-treatment. A process computer automatically controls the combustion process and keeps the thermal output of the system constant.

The kiln turns on roller bearings. The rocking motion produces a stoking effect which brings the oxygen needed for the incineration into close contact with the waste matter on the bottom of the kiln, thus ensuring its rapid and complete incineration. The kiln swivels on its own axis at an angle of approximately 90°.

The unique aspect of the rocking kiln system is that incinerators may be built in very small units with a capacity of 4 million BTU/hour but that can still handle 45-gallon drums. The largest unit by Von Roll has an 8.75 million BTU/hour capacity which, assuming an average waste BTU content of 6,000 BTU/lb equates to 5,000 tonnes a year capacity.

Previously, it was indicated that an 18.5 million BTU/hour capacity incinerator was planned and to achieve this for the Treatment Centre, a design incorporating two rocking kilns, as illustrated in Figure 2 and Figure 3, was chosen.

The flue gases (waste products from the incinerators) enter a pollution control train before being vented through the 20-metre stack to atmosphere.

The pollution control train was supplied by G.S. Ceilcote of Ohio as a complete system, capable of attaining emission specifications set by Chem-Security Ltd. in excess of that required to ensure compliance with the Operating Permit issued by the Alberta Department of Environment. The specifications are as follows.

The emissions at the stack shall not exceed:

		Concentration mg/m³
Total Particulates		35
Total Hydrogen Chloride	(HCl)	50
Total Sulfur Dioxide	(SO_2)	200
Total Hydrogen Fluoride	(HF)	2
Total Carbon Monoxide	(CO)	50
Total Hydrocarbons		25
Total P_2O_5		35

The Ceilcote unit accomplishes this by means of an Ionization Wet Scrubbing (IWS) facility that reduces the temperature of the hot incinerator flue gas down to 110°F by water scrubbing and removes particulates down to sub micron range by a combination of water scrubbing and electrostatic precipitation. The effluents from the unit comprises flue gas that will meet the specified air quality requirements, water that is injected down the deepweel, dilute acids, which are used in the phys/chem unit, and solid particles that are removed by filtration and placed in the secure landfill.

HIGH TEMPERATURE INCINERATOR

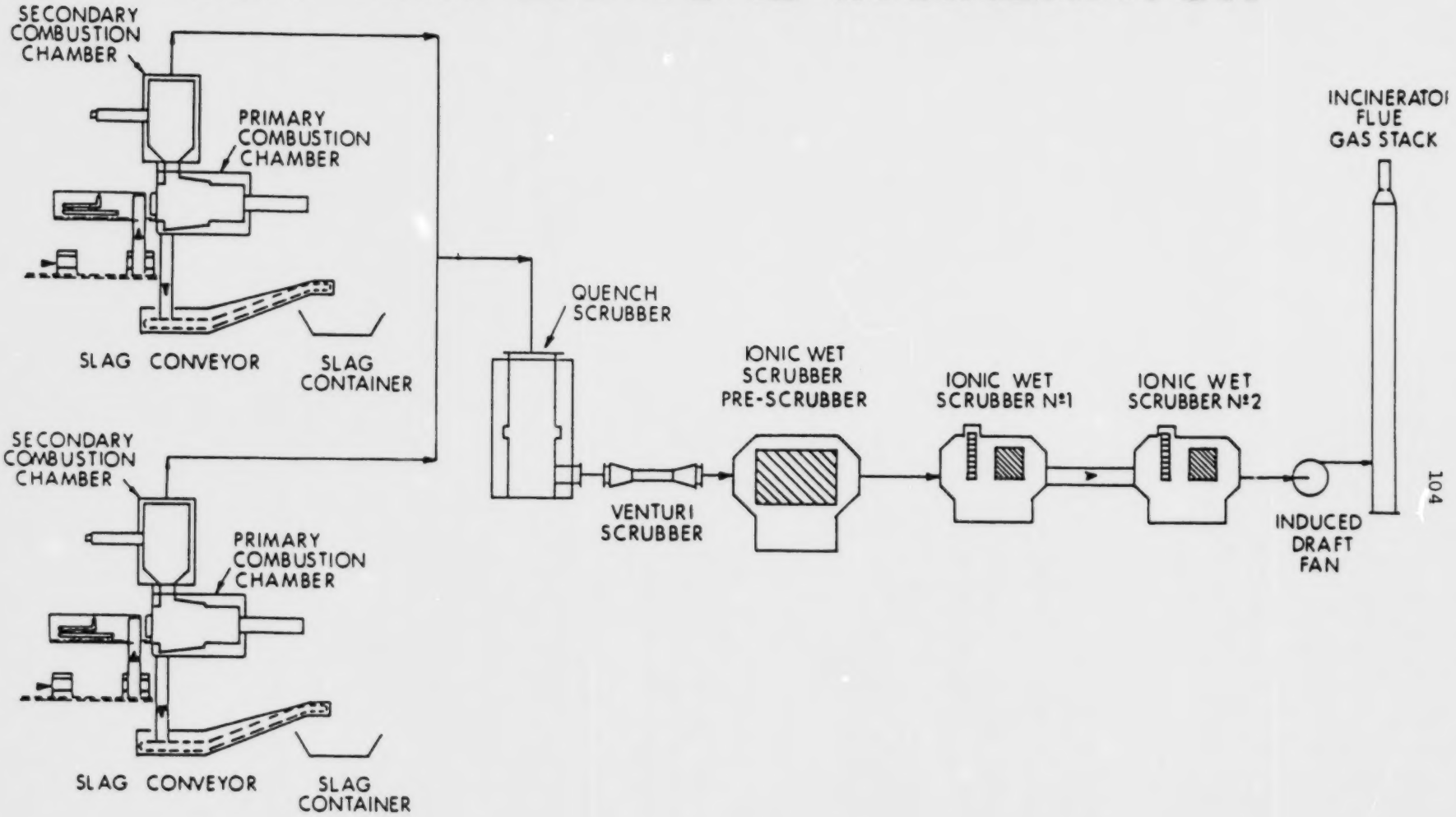


FIGURE 2

HIGH TEMPERATURE INCINERATOR

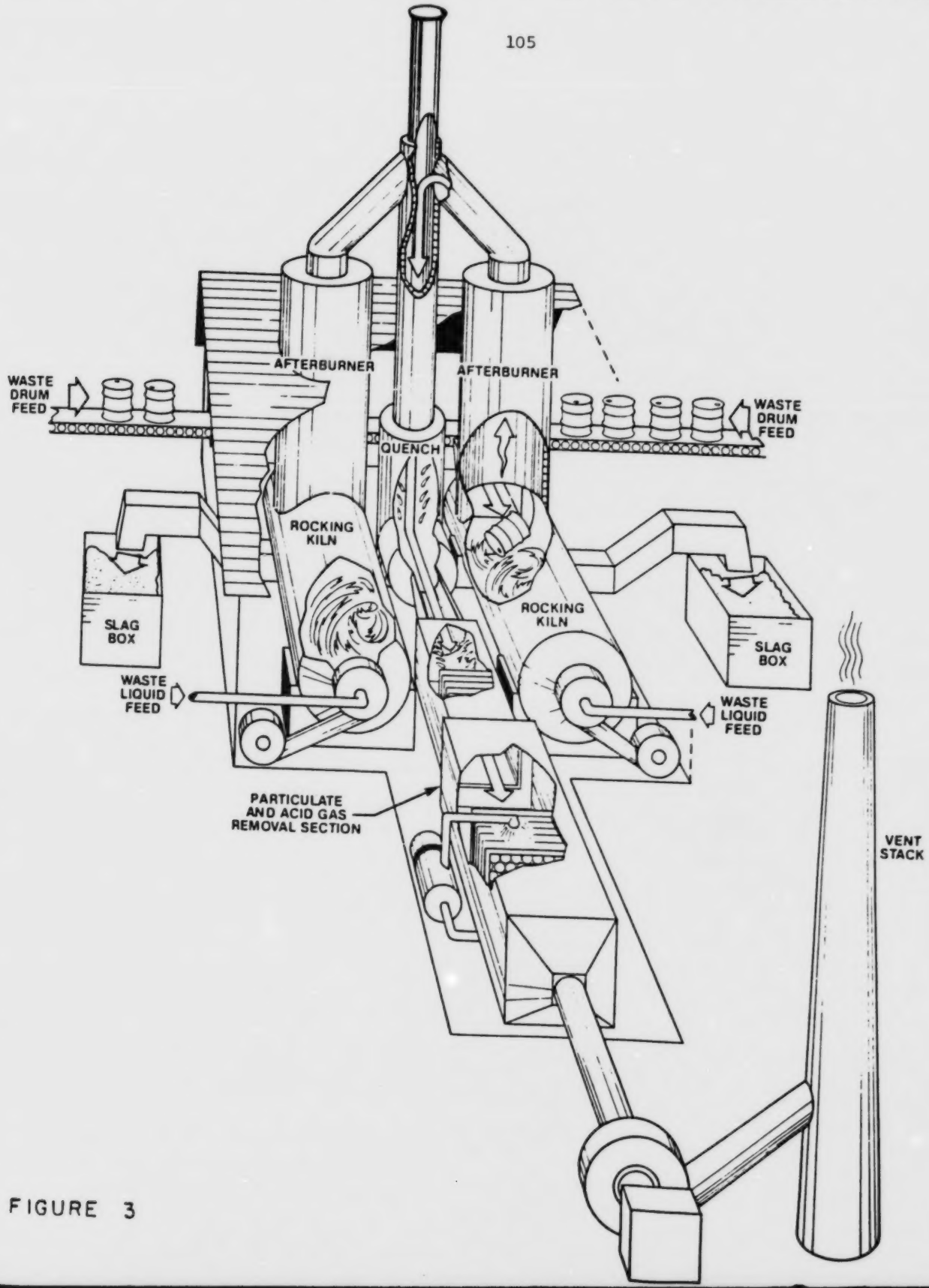


FIGURE 3

The system allows for excellent operational flexibility since, at no time, need the total incineration plant be down for maintenance, and it allows for one unit to be dedicated to a specific waste stream and thereby programmed for greatest combustion efficiency, leaving the other unit to handle the variations in feedstock BTU levels attributed to routine variations in waste receipts.

Additional units of 8.75 million BTU/hour incineration capacity can be added as required fairly readily, because of the modular nature of the construction of the rotating kiln furnace units, although consideration is now being given to a specialized 'roasting kiln' or 'desorber' for the processing of contaminated metal (from PCB transformers) and soils.

While not strictly a process facility, the organic storage tank farm is an integral part of the incineration system where liquid waste feed is blended in homogeneous batches in the tanks, each one capable of holding two tow-feed days operating feedstock. The organic storage tank form also comprises two receiving tanks, two storage tanks, a dedicated PCB storage tank, a water cut tank and a vent relief tank - fumes are ultimately vented to the incinerator.

The tank farm can accept bulk shipments, as illustrated in Figure 4, or can receive liquid wastes from the drum decant area in the waste receiving area, discussed later.

PHYS/CHEM TREATMENT PLANT

The Phys/Chem Treatment Plant is designed to treat up to 5,000 tonnes/year of inorganic waste based on a five-day week and single eight-hour shift. The wastes are received in liquid, sludge and solid forms and the plant is able to handle the range of substances varying as widely as waste acids, heavy metals and cyanides, in varying strengths and mixtures.

The plant comprises two discrete chemical reactor systems.

One system, which will usually treat alkaline waste and those containing cyanides or sulphides is fabricated from carbon steel lined with polytetrafluorethylene (PTFE). This design also enables it to be used, when required, to also treat extremely corrosive wastes.

The other system is built of fibreglass reinforced plastic with an internal coating of polypropylene. This system will treat the majority of the acid waste streams but as mentioned above highly corrosive wastes such as hydroflouric acid would be routed to the PTFE lined reactor.

Treatment capabilities of the plant include neutralization, precipitation, and oxidation/reduction.

Inorganic wastes are carefully evaluated to select the most appropriate treatment process. This selection process reduces sludge volumes and reagent consumption, consistent with personnel and equipment protection. Typically, waste treatment of inorganics commences in the reactor. All neutralization, oxidation and reduction processes are conducted in the reaction tank. Usually, the reactions that neutralize the waste are completed in aqueous solutions, and produce suspended solid precipitates and liquid by-products. These suspended solids are removed with a filter press.

The filtrate is pH-adjusted and subjected to further filtration prior to final disposal down the deep injection well, and the filter cake processed at the stabilization plant prior to deposition in the secure landfill cell.

ORGANIC STORAGE/INCINERATOR FEED TANK FARM

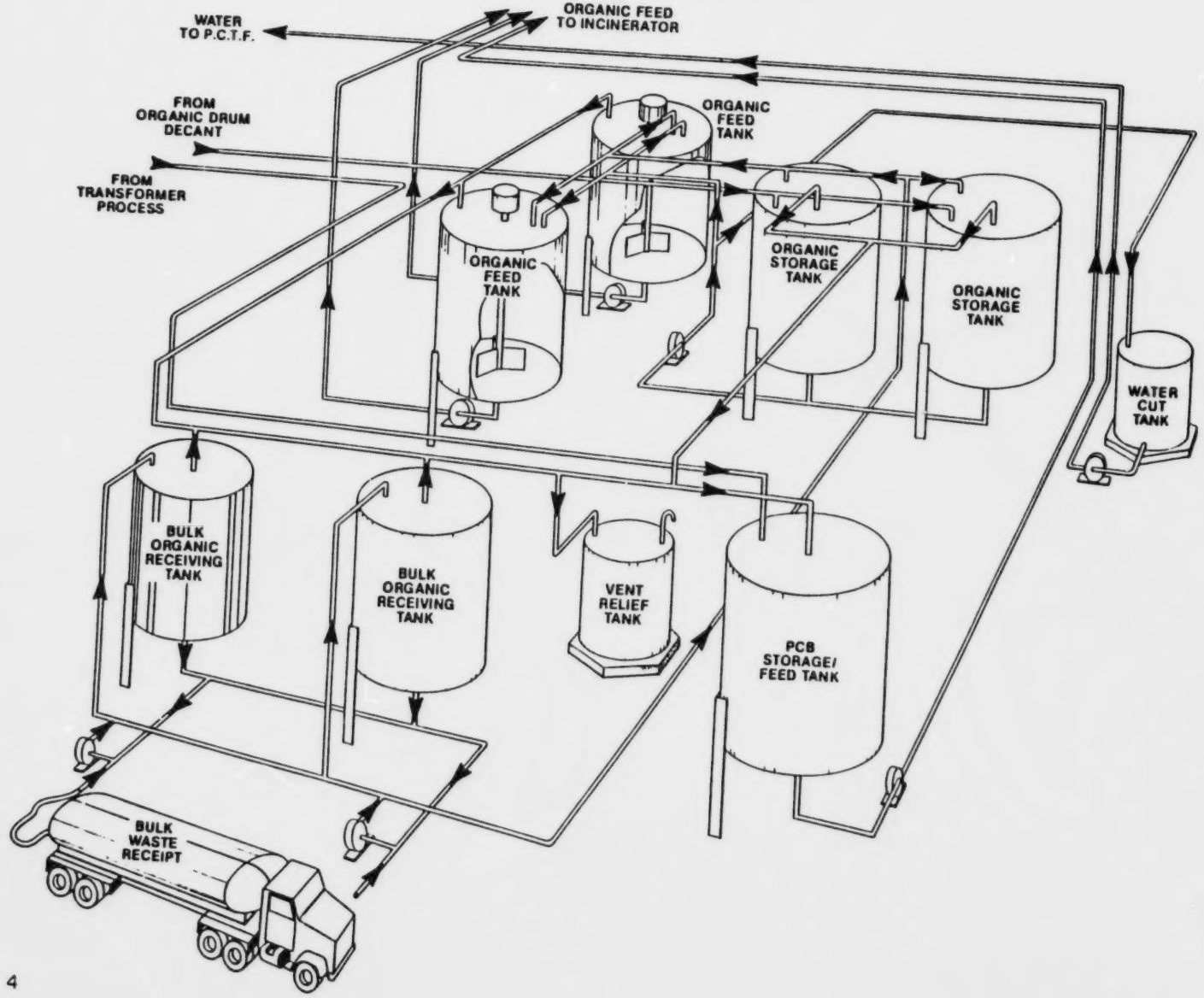


FIGURE 4

The phys/chem plant is illustrated in Figure 5.

STABILIZATION PLANT

The stabilization process is provided for treatment of residues and effluents from other waste processes and for treatment of wastes not suitable for either incineration or inorganic treatment. Stabilization comprises solidification and/or fixation. Fixation is a process whereby chemically reactive compounds such as cement are mixed with the water and other components in sludges and other aqueous wastes to form more stable solids such as concrete which both immobilizes and, in some cases, chemically changes the waste to render it non-toxic and non-leachable.

The stabilization plant comprises a series of feedhoppers for the stabilization materials and a storage pit from which the waste to be stabilized is fed to the 'pug mill' batch type mixer, as illustrated in Figure 6.

Chem-Security Ltd. is working with the Alberta Environmental Centre researching the most appropriate stabilization medium and testing protocols. Locally obtainable medium such as cement kiln dust or coal fired plant fly ash are being assessed as suitable cementation medium together with lime and Portland cement.

Whilst not considered processes, the landfill area and the injection deepwell are essential components of the Treatment Centre for the final disposition of process residuals.

SECURE LANDFILL

The landfill area is comprised of a series of trenches or cells designed to supplement the existing natural containment afforded by the extremely impervious clay - permeability of 10^{-6} cm/sec - 10^{-8} cm/sec - at the site. Engineered measures such as the installation of an 80 mm H.D.P.E. liner with associated network of leachate collection systems are further aided by a policy of ensuring only dry, stable materials are placed in the cells. The leachate collection system of which there are two - one above the liner and one below the liner - are constantly monitored. However, since no liquids are disposed of in the secure landfill and any active cell is completely covered by a rigid roof/structure, it is highly unlikely any leachate can be generated. Figure 7 gives a general indication of the design of a typical secure landfill cell.

INJECTION DEEPWELL

Deepwell injection of aqueous based wastes is a technique widely used in the Alberta oil and petrochemical industry. Liquid wastes are injected into suitable geological formations where they are isolated from any aquifer or portable water. This is a commonly used method of disposing of drilling fluids and saline wastes from oil exploration and production wells, and is also used by industry where the hydrogeology is appropriate to dispose of aqueous, usually saline, process wastes. In the case of the Treatment

PHYSICAL/CHEMICAL TREATMENT PLANT

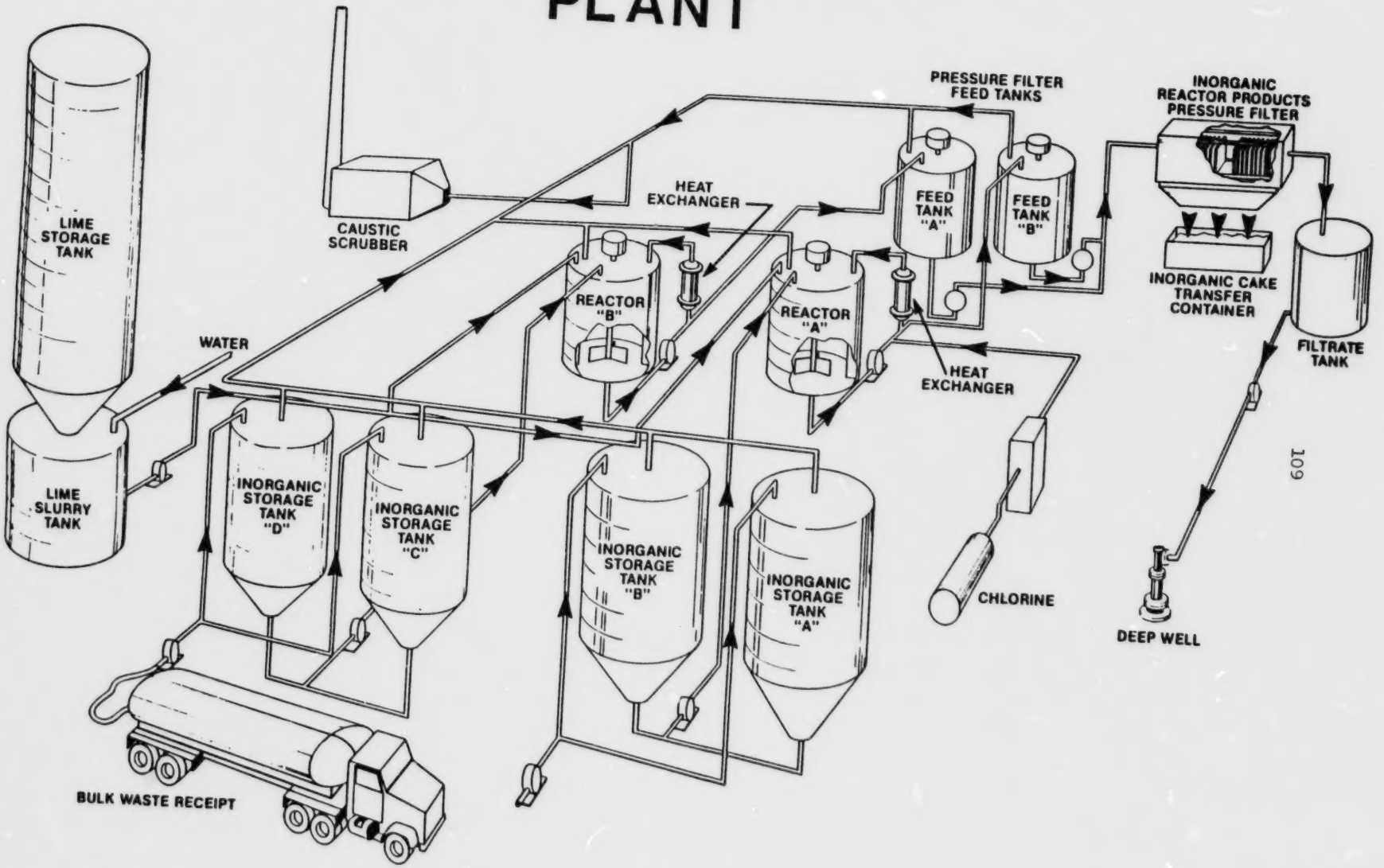


Figure 5

STABILIZATION / SOLIDIFICATION PLANT

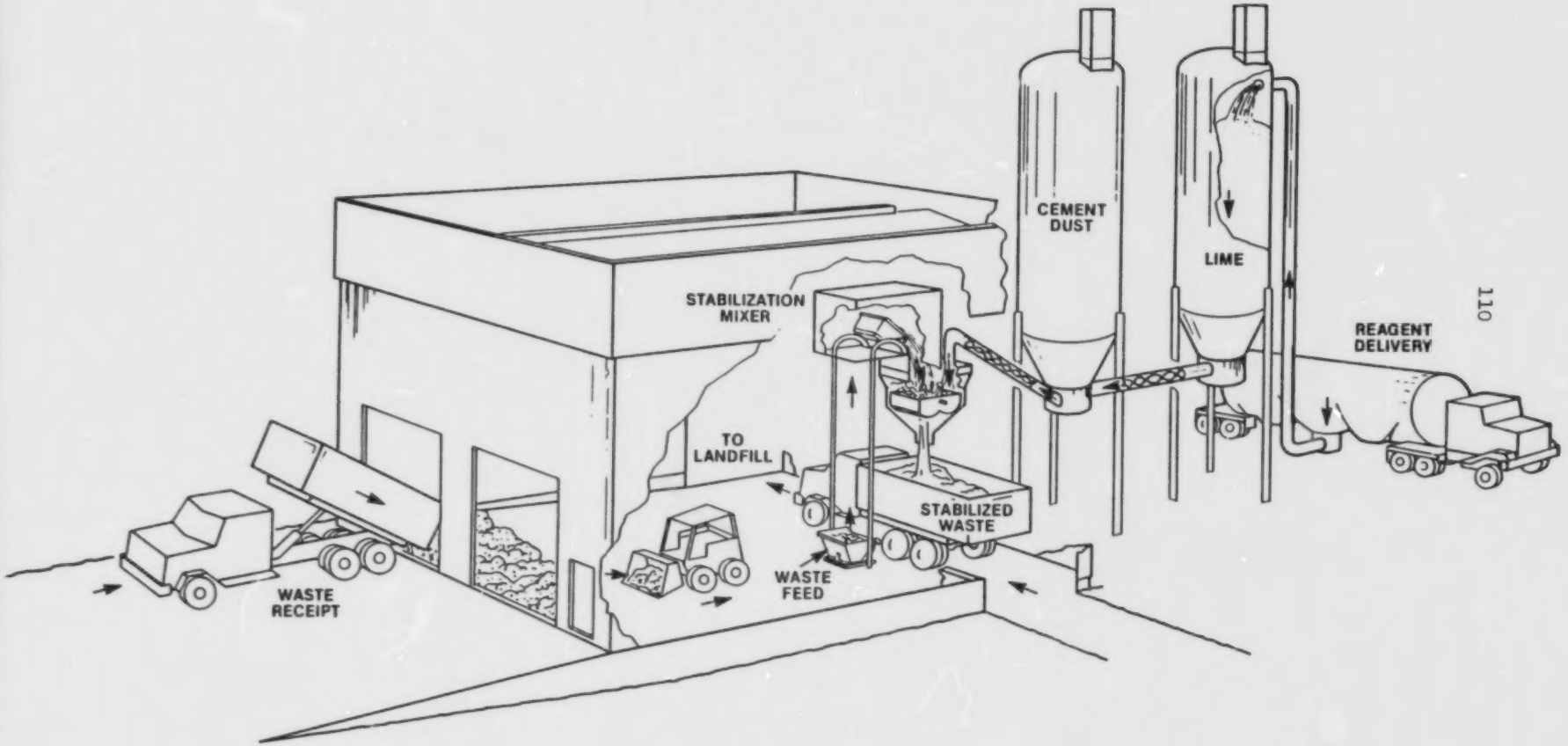


Figure 6

SECURE LANDFILL

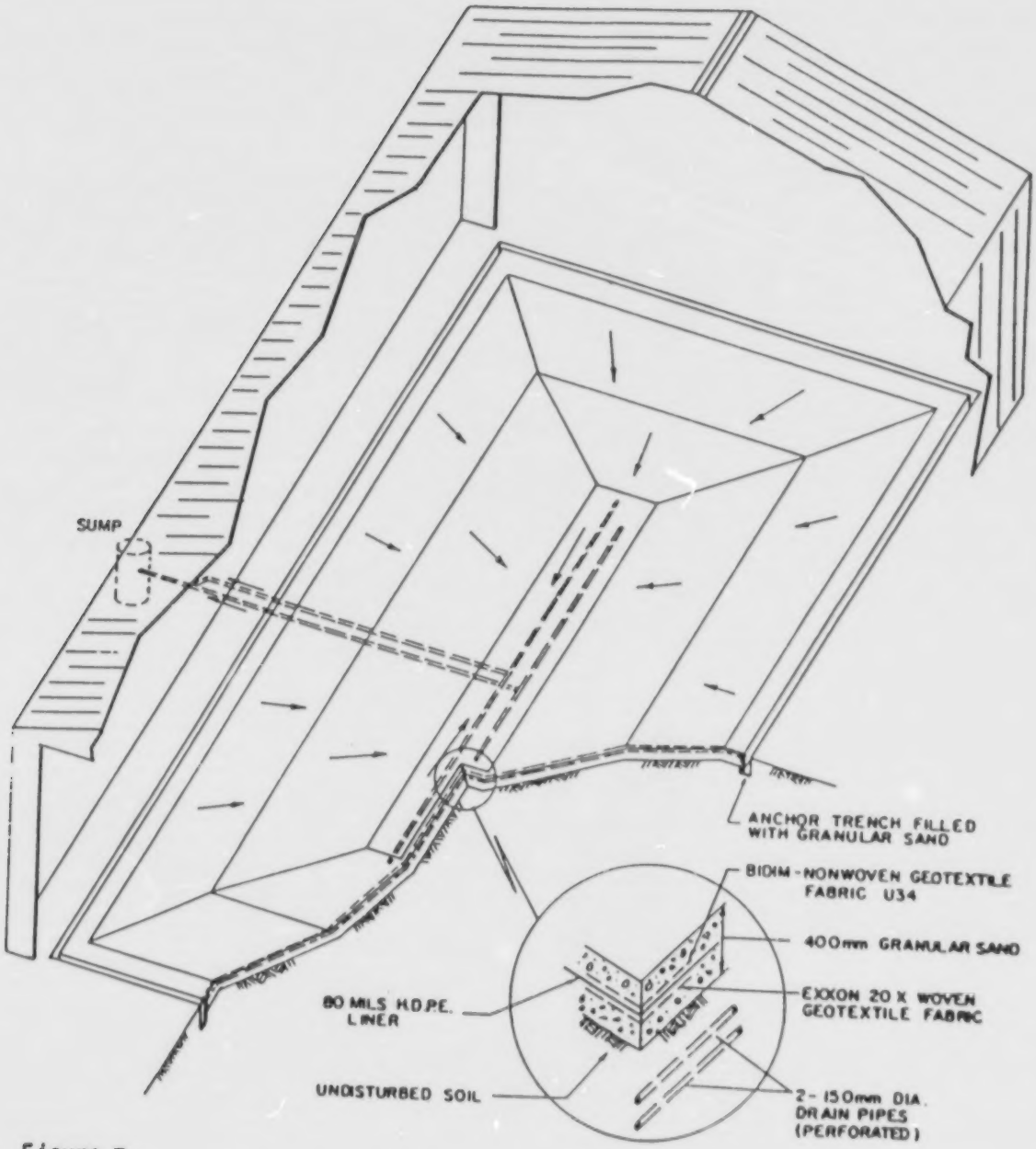


Figure 7

Centre, this method of disposal is limited to process waste water, treated waste water from the incinerator scrubber, site run-off water, and wash water from the truck decontamination system. The deepwell is not used for the disposal of any special or hazardous wastes.

The Treatment Centre deepwell has been drilled to a depth of 2,045 metres where the Winterburn Formation will be used as the injection zone. Test injection has indicated a zone capacity of up to 400 litres/minute at pressures in the order of 300 Kilo Pascals.

Prior to injection, waste water is pH-adjusted and filtered to ensure compatibility with the zone, in fact, the quality of water that is injected is, in many cases, of a higher standard than that in the zone.

STORAGE-CONTAINERS

Although the storage area set aside for wastes that constitutes the Treatment Centre feedstock is not a process, it warrants some review because of the unique approach taken to its design and integration with the Transportation and Collection Systems.

In our review of the Danish System it became apparent that such integration wash highly desirable, especially the resultant development of standardized shipping systems and containers.

Since Alberta does not have the extensive rail transportation network found in Denmark, an alternative for the safe movement of materials to the Treatment Centre had to be found that provided the excellent interim storage capacity of rail cars and used in that system.

The solution evolved from the review of the need for standardized containers at the smaller and mobile collection/transfer stations and the innovative design, that met the needs of all systems, was based on using a variation of an established transportation tool - sea-containers.

The modified container that Chem-Security Ltd. has designed is 20' x 8' x 4' with a removable bolted down lid. Each container will hold 36 45-gallon drums or a lesser number of liquid containers similar to the 500-litre units developed in Denmark.

The universal sea-containers may be used as unitized collection stations until filled, providing primary containment, where a designated Collection Centre does not have the necessary facilities.

In their primary role for general transportation between generators and the Treatment Centre, they are and excellent form of both unitized loads and secondary containment, providing the 'backup' system to the primary packaging or containment, and a good measure of protection in the event of a transportation incident.

The containers are also used in conjunction with small mobile laboratory/service centre when mobile collection 'milk runs' are conducted. In such a case, each mobile unit has a staff of one driver and one lab technician and comprise a tractor, one lab unit and one storage/shipping unit both located on a trailer bed. The trailer is fitted with a small lifting device/crane to both remove the container lids and load the containers. Thus making the mobile unit totally self-contained in the field.

Finally, at the Treatment Centre, the containers are used as interim storage for stockpiling wastes prior to either blending or treatment. Perhaps the greatest advantage of the containers is the ability to present a

clean tidy image to the public - there are no unsightly pile of rusted or dented drums, the signature of most treatment facilities.

The storage area at the Treatment Centre can handle up to one hundred containers for a feedstock storage capacity of 10-15 operating days. The containers, like their ocean-going counterparts, may be stacked up to three high for a total height of 13 feet using the 20-tonne bridge cranes located at the storage area which is also used for unloading other items and general duties as required.

STORAGE - WASTE RECEIVING BUILDING

Adjacent the storage area we have built a facility wherein containers full of drums are unloaded, the drums (containing liquids or pumpable sludges) are decanted and where the drums are shredded for ease of handling.

Figure 8 illustrates the general layout and key elements of this building, which, being the prime interface between the waste and the operators, is the site of the highest potential health hazard. It is for this reason that a great deal of attention has been given to the design of this facility.

The building in general undergoes 12 air changes an hour and fume hood devices are used at site specific locations such as the shredder (which has in addition, a steam blanket over the operation to preclude any fire/ignition hazard) and the individual decant nozzles.

The exhaust from the fume hoods are passed through a wet scrubber to ensure compliance with emission standards.

In addition to processing empty drums, the shredder can be used to process frozen drums or solidified drums of inorganic or organic wastes. The shards or shredded pieces are then either put into an empty drum either to allow it to thaw (inorganic) or for transfer along the conveyor system to the incinerator.

Also, PCB filled transformers that have been previously flushed clean may, after preliminary dismantling, be shredded, and the resultant shards of copper and steel passed through the proposed 'roasting' kiln to reclaim the metals.

FUTURE PLANS

As was mentioned in the preceding paragraph, it is planned to add a 'roasting' kiln, to allow for the cost effective treatment (by decontamination) of soils and certain inorganic/organic sludges and recycling of the metals in PCB transformers.

In addition, the construction of specific facility for the dismantling of PCB transformers and a large more powerful shredding machine - to handle the larger transformers and reactors - is being assessed.

Further plans include the expansion and automation of the stabilization plant, to reduce the heavy manpower demands of that operation.

STORAGE-WASTE RECEIVING BUILDING

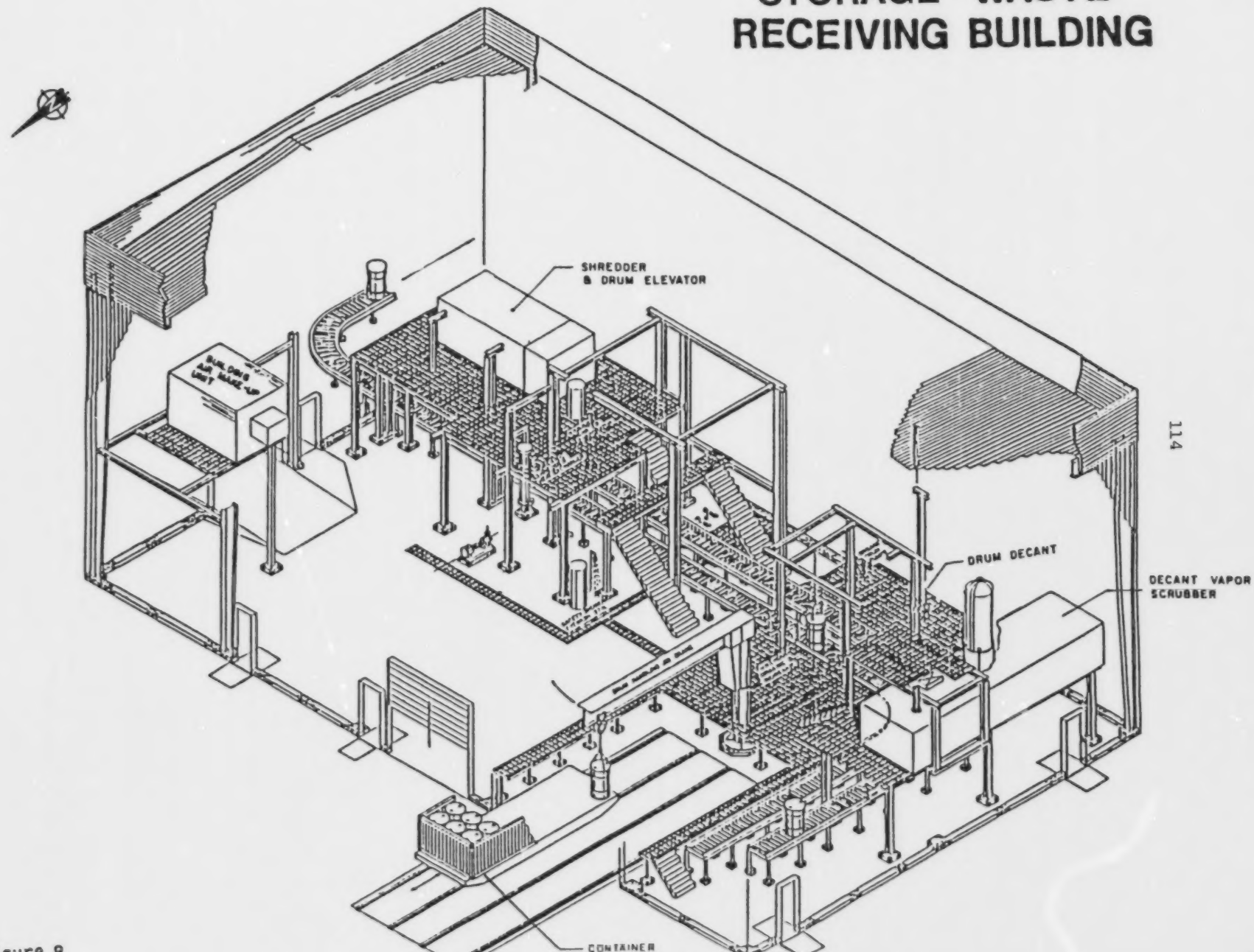


Figure 8

LA MODÉLISATION PHYSIQUE: UNE MÉTHODE UTILE EN VUE DE RÉDUIRE LES ÉMISSIONS DE HAP D'UNE ALUMINERIE À TECHNOLOGIE SODERBERG

Richard Gilbert

Société d'Électrolyse et de Chimie Alcan Ltée
C.P. 1500
Jonquière (Québec) Canada G7S 4L2

Jean-Louis Laforte

Université du Québec à Chicoutimi
555 Boul. Université
Chicoutimi (Québec) Canada G7H 2B1

RÉSUMÉ

Le présent exposé décrit les résultats d'expérimentation sur des modèles physiques, aux laboratoires de l'Université du Québec à Chicoutimi, dans le cadre d'un projet de la Société d'Électrolyse et de Chimie Alcan visant à augmenter l'efficacité de captation des goudrons du procédé d'épuration à voie humide.

Trois (3) solutions d'améliorations ont été étudiées en détail, soient: la rectification de l'écoulement des gaz à l'entrée de l'épurateur industriel, l'amélioration de la captation mécanique des goudrons par des jets de liquide haute pression et finalement l'utilisation de la haute tension en milieu humide. Les modèles physiques ont permis d'identifier des solutions prometteuses qui serviront pour la construction d'un épurateur industriel prototype.

INTRODUCTION

Depuis plusieurs années, la Société d'Électrolyse et de Chimie Alcan Ltée (SÉCAL) a entrepris au Québec un vaste programme de recherche et de développement pour réduire les émissions atmosphériques de goudrons de ses salles de cuves de technologie Soderberg. Le programme global vise tout d'abord à réduire la génération de goudrons à la source, en utilisant des mélanges de pâte améliorés. Dans une deuxième étape, on cherche à augmenter l'efficacité du procédé d'épuration des gaz de cuves. Le présent exposé portera uniquement sur ce dernier aspect.

Le développement et la mise au point d'une technologie d'épuration sur des unités industrielles comportent des difficultés considérables. Les essais en usine doivent être de longue durée pour être représentatifs et il n'est pas économiquement possible d'expérimenter en usine toutes les solutions potentiellement envisageables car les coûts de toutes ces modifications sont prohibitifs. Il devient alors avantageux d'utiliser des techniques de modélisation physique. Cette méthodologie a été utilisée pour identifier les solutions susceptibles

d'améliorer la technologie d'épuration humide Alcan.

ESSAIS DE RECTIFICATION DE L'ÉCOULEMENT DES GAZ

La première amélioration étudiée en laboratoire a été la rectification de l'écoulement des gaz à l'entrée de l'épurateur industriel. Dans les épurateurs existants, l'entrée des gaz est perpendiculaire à la tour de lavage ce qui entraîne que le profil des gaz a l'aspect reproduit à la figure 1; une telle distribution rendrait difficile l'implantation des améliorations envisagées; il faut donc le corriger. [1] On remarque que la vitesse varie fortement par rapport à la valeur moyenne de 1,4 m/s. Les fluctuations atteignent jusqu'à 4 fois la vitesse moyenne lorsqu'on se situe à 2 mètres de la paroi opposée à l'arrivée des gaz. Pour être considérées acceptables, les variations de vitesse dans les différentes sections de l'épurateur ne devraient pas excéder 20% de la vitesse moyenne.

Afin d'améliorer l'écoulement des gaz à l'entrée de l'épurateur industriel, un modèle physique a été construit. La figure 2 présente un schéma du modèle physique à l'échelle 1:17, comprenant un ventilateur de 15 HP, un conduit d'amenée des gaz et un corps cylindrique représentant l'épurateur industriel. La partie inférieure de l'unité cylindrique présente une fenêtre amovible en plexiglass permettant de voir à l'intérieur de même que d'accéder rapidement dans la région où sont installées les différentes composantes du système de rectification des gaz. Le montage comprend également une pièce de contreplaqué simulant le niveau de liquide, un éliminateur de gouttelettes et une cheminée.

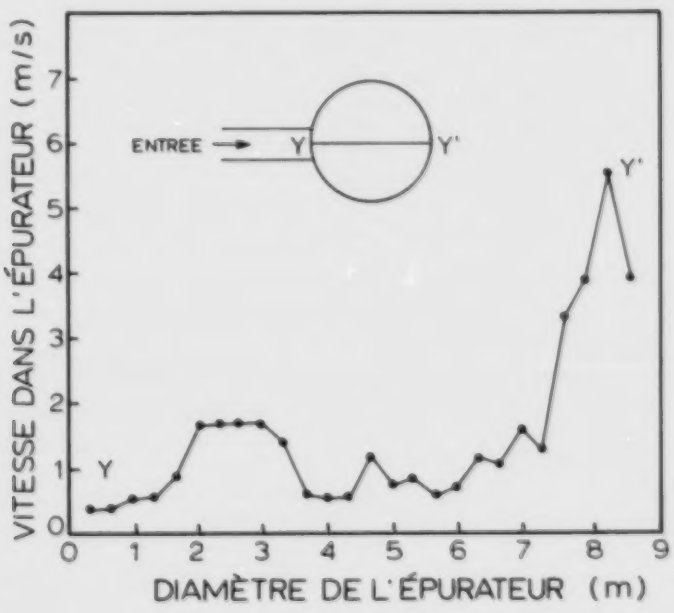


FIGURE 1: PROFIL DE VITESSE MESURÉ À L'INTÉRIEUR DE L'ÉPURATEUR INDUSTRIEL DE 9 m DANS LA DIRECTION FACE AU CONDUIT

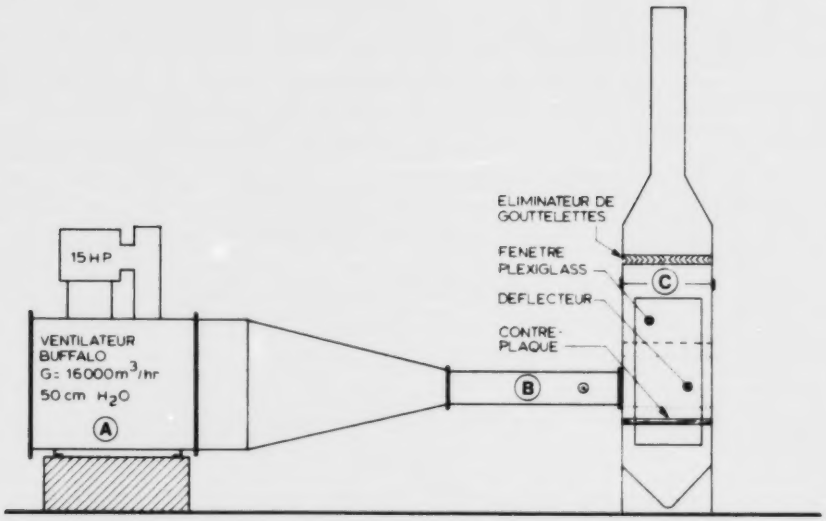


FIGURE 2: SCHÉMA DU MODÈLE PHYSIQUE SIMULANT L'ÉCOULEMENT DES GAZ DE L'ÉPURATEUR INDUSTRIEL SECAL
A) Ventilateur
B) Conduit d'amenée des gaz
C) Corps cylindrique

Dans ce modèle physique, seul l'écoulement des gaz est simulé, et pour cette raison, aucun liquide n'est utilisé. Au total, 127 systèmes de rectification ont été étudiés sur une période de quatre (4) mois.

Les profils de vitesses ont été mesurés à 13,5 cm au-dessus du conduit d'amenée des gaz, soit une position équivalente à une hauteur de 2,6 m dans l'épurateur industriel.

La figure 3 montre l'amélioration obtenue avec le meilleur système de rectification expérimenté [2]. La courbe en traits pleins correspond au profil de vitesses mesurées sans aucun système de rectification. Cette courbe s'apparente fortement à celle obtenue à l'entrée de l'épurateur industriel. Pour sa part, la courbe en traits pointillés est celle obtenue en maquette avec le meilleur système de rectification qui est constitué de quatre (4) vannes déviatrices situées à l'extrémité du conduit d'amenée des gaz, de vingt-six (26) ailettes verticales dans le corps cylindrique ainsi que d'un écran diffuseur situé au-dessus des ailettes.

Avec ce système, les fluctuations de vitesse sont inférieures à 20% par rapport à la vitesse moyenne. Cette valeur étant jugée acceptable, les essais d'optimisation se sont poursuivis pour améliorer la captation mécanique des goudrons.

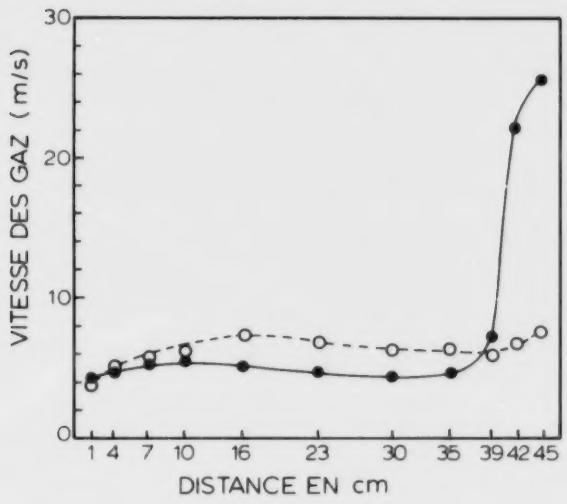


FIGURE 3: COMPARAISON DES PROFILS DE VITESSE MESURÉS DANS LE MODÈLE PHYSIQUE
O———O sans système de rectification (traits pleins)
X-----X avec système de rectification optimisé (traits pointillés)

ESSAIS D'AMÉLIORATION DE CAPTATION MÉCANIQUE DES GOUDRONS

Les émissions atmosphériques de goudrons comptent parmi les particules les plus difficiles à capter dans les épurateurs humides, en raison principalement de la taille sub-micronique de ces particules.

La figure 4 montre l'efficacité de captation mesurée sur un épurateur industriel Sécal en fonction de la taille des poussières (courbe en traits pointillés) [3]. Sur cette figure, apparaissent également (en traits pleins) les courbes d'efficacité correspondant à différents épurateurs à voie humide commerciaux qui présentent trois (3) niveaux de rendement: faible, moyen et élevé, selon l'énergie croissante consommée [4]. D'après cette figure, on se rendra compte que l'efficacité de l'épurateur industriel Sécal correspondrait à celle d'un épurateur de faible rendement et qu'il pourrait être possible d'augmenter son efficacité sur les goudrons en améliorant la captation mécanique par les gouttelettes d'eau.

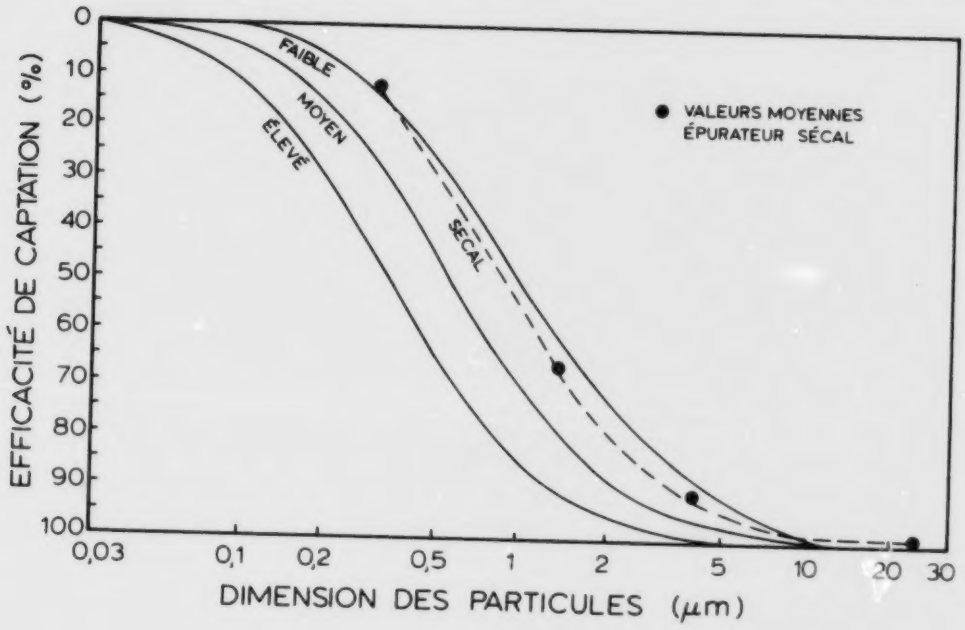


FIGURE 4: EFFICACITÉ DE CAPTATION MÉCANIQUE DES PARTICULES SELON LEUR DIAMÈTRE POUR DIFFÉRENTS TYPES D'ÉPURATEURS HUMIDES

Pour vérifier cette hypothèse, un modèle physique a été construit en laboratoire pour simuler le mécanisme de captation mécanique [5]. Il s'agit d'une unité cylindrique de 45,7 cm de diamètre, traitant environ 1/300 du volume des gaz circulant dans l'épurateur industriel.

La figure 5 présente un schéma du modèle physique utilisé montrant le ventilateur, l'unité de préchauffage des gaz à 75°C, le générateur de goudrons et le système de recirculation des liquides.

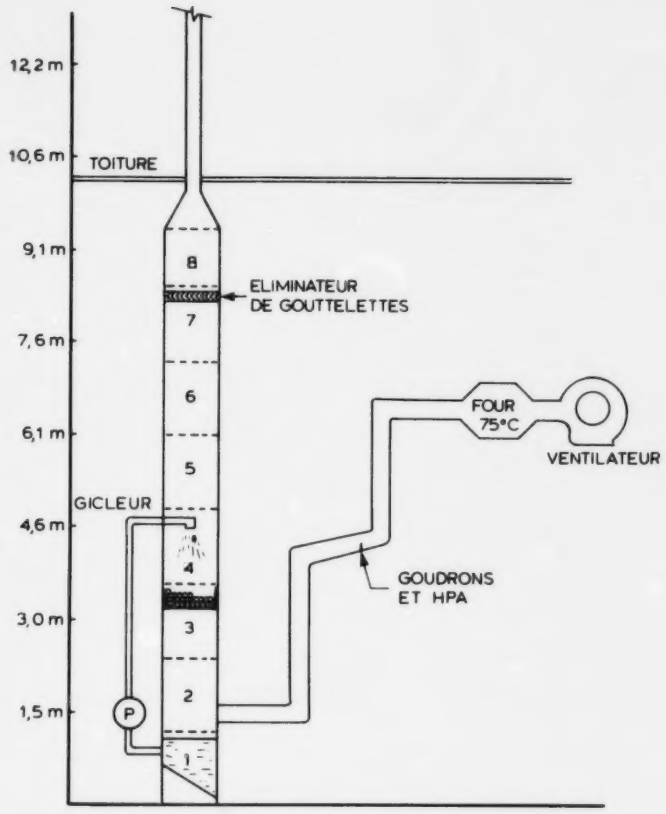


FIGURE 5: SCHÉMA DU MODÈLE PHYSIQUE SIMULANT LA CAPTATION MÉCANIQUE DES GOUDRONS PAR DES JETS DE LIQUIDE

Le tableau 1 identifie les caractéristiques de ce modèle physique. Contrairement au modèle décrit précédemment, le montage n'a pas été construit à l'échelle exacte de l'épurateur industriel. On s'est assuré plutôt qu'il reproduise fidèlement les paramètres physiques responsables de la captation mécanique, c'est-à-dire la même vitesse des gaz à l'entrée, à l'intérieur du corps cylindrique et dans la cheminée ainsi que la même pression aux gicleurs et le même rapport du débit de liquide au volume de gaz traité. Les essais effectués avec le montage ont consisté d'abord à valider l'efficacité de captation sur les goudrons par rapport à l'épurateur industriel et ensuite à vérifier comment l'augmentation de la pression du gicleur influence l'efficacité de captation des goudrons.

TABLEAU 1: CARACTÉRISTIQUES DU MODÈLE PHYSIQUE DE CAPTATION MÉCANIQUE DES GOUDRONS

CARACTÉRISTIQUES DU MODÈLE PHYSIQUE		FACTEUR D'ÉCHELLE
Diamètre du cylindre	45,7 cm	1:17
Débit des gaz à 75°C	22,7 m^3/min	1:300
Vitesse moyenne des gaz dans la partie centrale	2,0 m/s	1:1
Vitesse des gaz dans le conduit d'entrée	12,6 m/s	1:1
Vitesse des gaz dans la cheminée	14,3 m/s	1:1
Débit de liquide de recirculation	43,0 l/min	1:300
Pression au gicleur	0,07 MPa	1:1

La figure 6 montre l'efficacité de captation des goudrons en fonction de la pression au gicleur [5]. L'efficacité de captation des goudrons obtenue par modélisation physique atteint 7% pour une pression au gicleur de 0,07 MPa. Ceci est comparable à l'erreur expérimentale près à la valeur de 11% obtenue avec l'épurateur humide industriel. Pour une pression plus élevée, soit 0,27 MPa, la captation des goudrons augmente à 26%. Il apparaît donc possible d'améliorer l'efficacité de captation des goudrons en augmentant la pression au gicleur. À titre d'exemple, pour une pression de 0,5 MPA, ce qui nécessite une puissance additionnelle de 200 HP, il serait possible d'obtenir une efficacité d'environ 35% sur les goudrons. Une telle efficacité constituerait une amélioration intéressante par rapport à l'efficacité actuelle; il faut cependant évaluer des moyens d'aller plus loin, et, pour cela, nous nous sommes tournés vers une autre technologie, la technologie électrostatique.

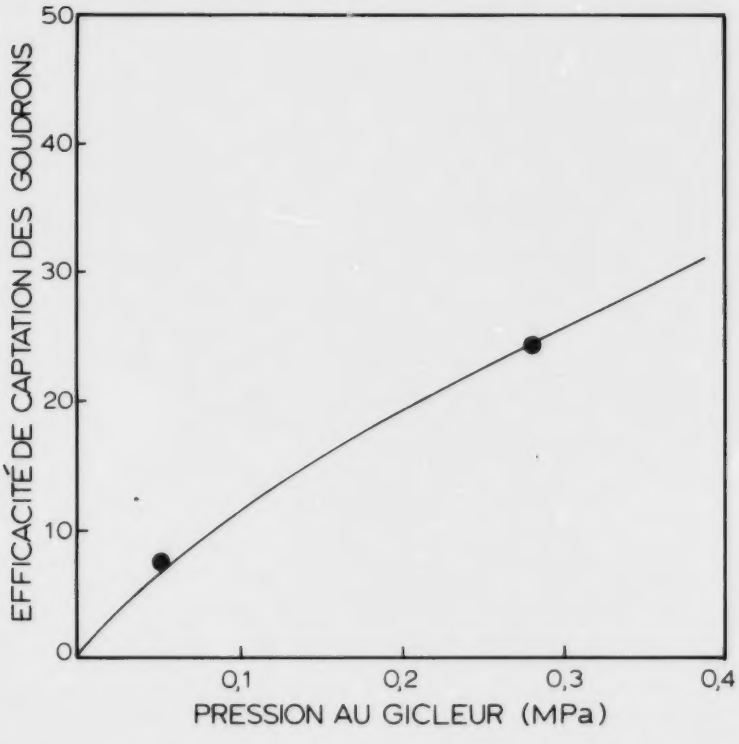


FIGURE 6: EFFICACITÉ DE CAPTATION DES GOUDRONS EN FONCTION DE LA PRESSION AU GICLEUR

ESSAIS D'AMÉLIORATION DE CAPTATION ÉLECTROSTATIQUE DES GOUDRONS

Si les épurateurs humides sont relativement peu performants pour capter les goudrons en raison de leur taille sous-micronique, ces derniers sont également plus difficiles à capter que les autres poussières avec les technologies électrostatiques, à cause de leur faible constante diélectrique. Il existe plusieurs publications décrivant diverses techniques électrostatiques pour augmenter la captation des goudrons en milieu humide. Certaines solutions d'amélioration consistent à capter les goudrons au moyen de gouttelettes chargées [6-7]. D'autres techniques plus couramment utilisées consistent à charger les particules de goudrons à l'aide d'électrodes à haute tension et à attirer ces particules sur des plaques collectrices [8-9-10].

Un modèle physique visant à étudier les différentes solutions électrostatiques a été construit en laboratoire [11-12]. Parmi toutes les solutions expérimentées, celle qui s'est avérée la plus efficace est celle utilisant les plaques collectrices et les électrodes à haute tension.

La figure 7 montre de façon schématique le modèle physique ayant servi à l'expérimentation. Le montage de base comprend les mêmes composantes que celui déjà décrit utilisé pour étudier la captation mécanique. Il comprend, en plus, une unité électrostatique constituée de deux (2) conduits rectangulaires de 20,3 X 40,6 cm et de 4,8 m de hauteur dont les parois forment les plaques collectrices de 11,8 m^2 de surface. Les électrodes émissives de haute tension sont placées au centre des deux (2) conduits. La haute tension est appliquée au sommet du montage à l'aide d'une source pouvant générer un voltage maximum de 100 KV.

Le liquide utilisé lors des essais pour laver les plaques collectrices était soit de l'eau du robinet ou de la liqueur provenant de l'épurateur industriel.

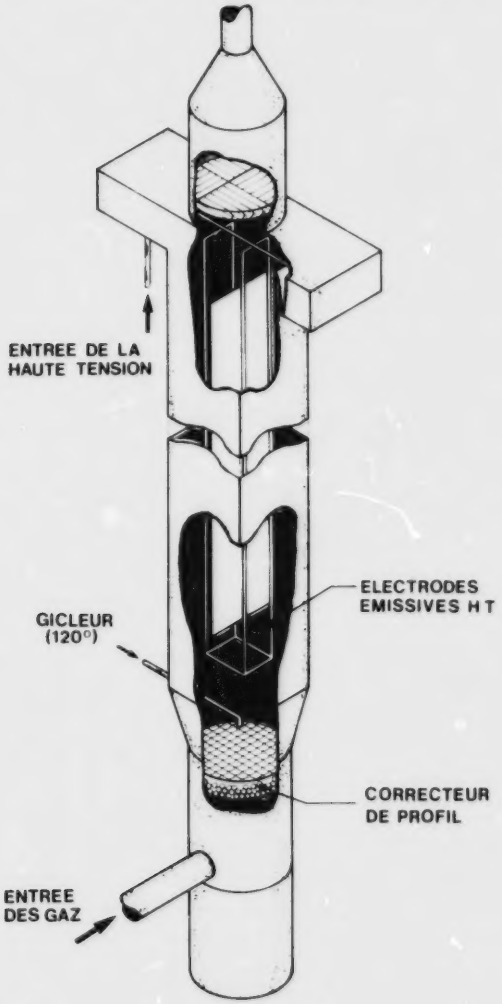
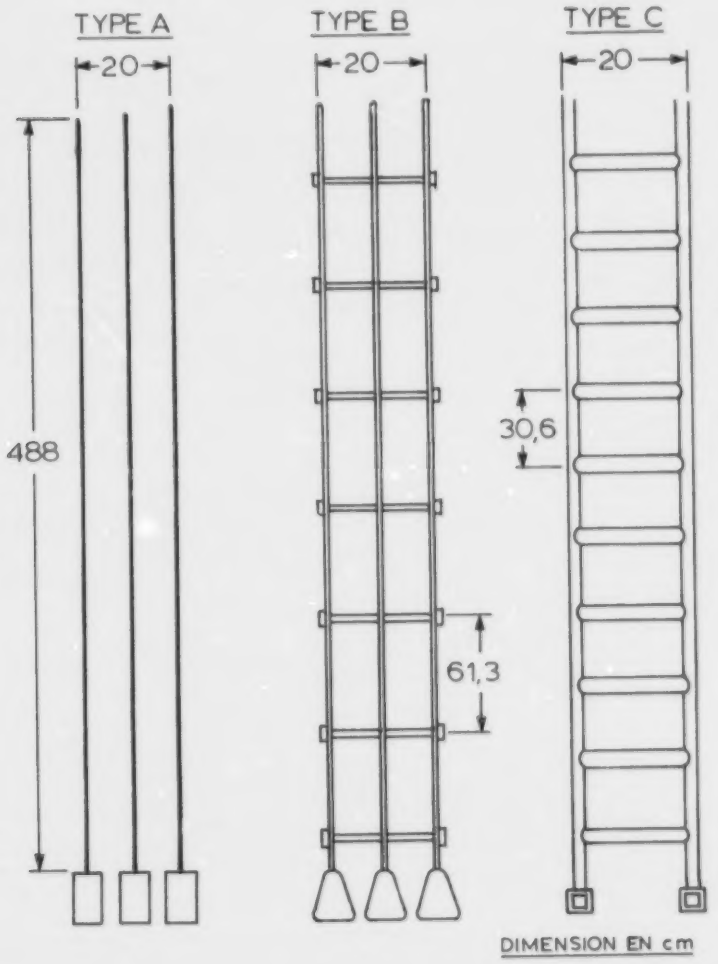


FIGURE 7: SCHÉMA MONTRANT LE MODÈLE PHYSIQUE UTILISÉ POUR ÉTUDIER LA SOLUTION ÉLECTROSTATIQUE UTILISANT LES PLAQUES COLLECTRICES ET LES ÉLECTRODES À HAUTE TENSION

Quelques 150 essais portant sur la captation des goudrons ont été complétés avec le montage décrit précédemment. Quatre (4) types d'électrodes ont été expérimentés. Un schéma de ces électrodes est présenté à la figure 8 et les résultats des essais au tableau 2. À partir des données de ce tableau, on constate que seulement les électrodes C et D sont satisfaisantes en raison de leur stabilité aux vibrations. D'autre part, le courant débité avec ces électrodes atteint 40 nA/cm^2, ce qui est comparable aux valeurs généralement rencontrées dans les précipitateurs électrostatiques industriels.



TYPE D: Même assemblage que le type C avec, en plus, quatre fils multibrins attachés le long de chacun des tubes cylindriques.

FIGURE 8: SCHÉMA DESCRIPTIF DES QUATRE TYPES D'ÉLECTRODES EXPÉRIMENTÉS

TABLEAU 2: RÉSULTATS DES ESSAIS POUR QUATRE (4) TYPES D'ÉLECTRODES ÉMISSIVES

TYPE D'ÉLECTCRODES	VOLTAGE MAXIMUM APPLIQUÉ Sec kV	Humide kV	REMARQUES Vibration	Oscillations
A. Fil de 4,9 mètres avec poids	-40	-35	Grande	Grande
B. Lame d'acier	-40	-35	Grande	Grande
C. Tubes d'acier (16 mm)	-55	-50	Très petite	Très petite
D. Tubes d'acier avec fil	-55	-55	Très petite	Très petite

La performance de l'unité électrostatique a été mesurée dans différentes conditions de voltage, de vitesse des gaz et de débit de lavage.

La figure 9 présente les résultats d'efficacité obtenus en fonction de la tension appliquée pour différents débits de lavage avec l'eau et la liqueur d'épuration. Ces résultats montrent clairement la grande amélioration de captation à mesure qu'on augmente la tension appliquée. Lors des essais en laboratoire, la tension maximale appliquable atteignait 50 KV avec de l'eau et 45 KV avec la liqueur d'épuration. Nous obtenions alors des efficacités de captation des goudrons de l'ordre de 80 à 90%. Les essais réalisés avec le modèle physique indiquent également que l'efficacité d'une unité électrostatique dépend fortement de la surface de plaques collectrices qu'il est possible de loger dans l'épurateur industriel. Pour cette raison, il n'est pas possible de prédire exactement l'efficacité de captation pour une unité industrielle. Signalons pour terminer que les essais de modélisation électrostatique en laboratoire donnent généralement des résultats d'efficacité supérieurs à ce qu'on obtient sur des unités industrielles.

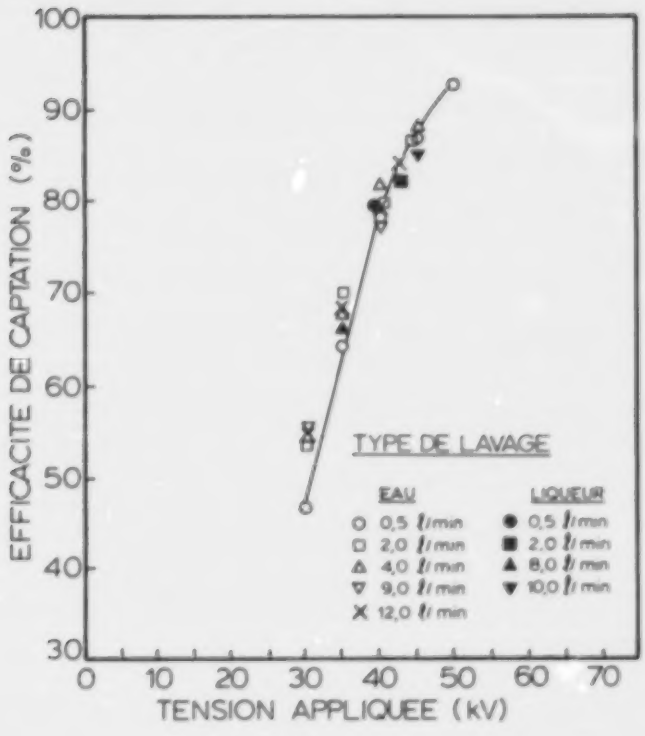


FIGURE 9: EFFICACITÉ DE CAPTATION DES GOUDRONS DE L'UNITÉ ÉLECTROSTATIQUE POUR DIFFÉRENTS DÉBITS DE LAVAGE À L'EAU ET À LA LIQUEUR

CONCLUSIONS

Les travaux de modélisation physique effectués à l'Université du Québec à Chicoutimi ont permis de sélectionner rapidement les options les plus intéressantes pour améliorer la technologie d'épuration humide des gaz de cuves Soderberg.

Les résultats encourageants de ces travaux ont conduit la Société d'Électrolyse et de Chimie Alcan à envisager l'application de ces options en commençant par améliorer la répartition des gaz d'un épurateur industriel. Celui-ci a ensuite été équipé avec un système de pulvérisation à haute pression. En parallèle, les tests se poursuivent pour préciser le type de matériaux utilisables dans la mise en place d'une unité électrostatique à l'intérieur de cet épurateur.

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HARBOR DREDGING: TWO EXAMPLES OF THE AMERICAN EXPERIENCE (CHICAGO AND WAUKEGAN HARBORS)

By

Dr. Philippe Ross
Illinois Natural History Survey, US

Paper unavailable at time of printing

THE INCINERATION OF LOW LEVEL RADIOACTIVE WASTES

Jack D. Lauber, P.E.
Bureau of Air Toxics
New York State Department of Environmental Conservation
Albany, New York 12233-3255

Presented April 7, 1988 Conference
on Toxic Substances Sponsored by the Air Pollution
Control Association, Environment Quebec, and
Environment Canada, Montreal Quebec, Canada

Low level radioactive wastes (LLRW) are increasing in volume, coming from medical and academic institutions, nuclear power plants, and industrial firms. Most LLRW are now shipped to only a few special disposal facilities in Washington and South Carolina in the United States. Federal law requires the states to develop their own treatment and disposal facilities by 1993.

Many categories of LLRW are incinerable and subject to volume reduction by waste incineration, which should be considered a viable waste disposal option. No full scale commercial LLRW incineration facility yet exists in the United States; however, such a state-of-the-art volume reduction LLRW incineration facility is being planned for Pennsylvania, based to a large extent on the design and operation of the Los Alamos, New Mexico National Laboratory Transuranic waste incinerator, which is a good example of best demonstrated technology which will be discussed in this paper. Other examples of the applications of state-of-the-art incineration methods for volume reduction of LLRW are presented.

There has been certain public concern about the safety of LLRW incineration, especially for trace toxic and radioactive emissions. State-of-the-art multi-stage controlled air incineration with high efficiency air cleaning systems that can fully control all toxic emissions, are discussed.

Introduction

We generally hear much about the problems of disposing of hazardous wastes in our environment - an important national concern and challenge.

Low level radioactive wastes (LLRW) are another aspect of this important problem. Large volumes of such wastes are generated from nuclear power plants, industries, hospitals, medical and research institutions. At present, some of this biomedical waste is either incinerated on site in less than state-of-the-art hospital incinerators, or buried at a few commercial special LLRW disposal facilities.

Mixed wastes, such as RCRA (Resource Conservation and Recovery Act) type hazardous waste solvents, etc., and LLRW are another special problem, especially from Department of Energy military type facilities.

Large scale incineration of LLRW can accomplish large degrees of waste volume reduction. The use of BDAT (best demonstrated available technology), and LAER (lowest achievable emission rate), air pollution control systems can both properly control conventional, trace toxic (e.g., dioxin) and radioactive air contaminants. Examples of certain existing and proposed LLRW incineration facilities will be presented.

Low Level Radioactive Waste Generation[1]

The term LLRW is a general term for a very wide range of radioactive wastes which come from nuclear industries, hospitals, and medical research institutions both in the public and private sectors. LLRW consists of the radioactive materials themselves and other materials, such as oils and solvents which have become contaminated by contact with radioactive materials. Solid low level wastes can also be paper, wood, plastics, biological materials, etc. contaminated with radionuclides.

Presently, there are more than 20,000 companies, installations, laboratories, and government facilities that are licensed by the U.S. Nuclear Regulatory Commission to use radioactive materials. It has been estimated that about 128 million cubic feet of LLRW will be generated from 1980 to the end of this century.[1] New York State for example generated 107,750 cubic feet of LLRW in 1986.[4]

The types of low level radioactive waste generated by nuclear fuel cycle power plants, both for boiling water and pressurized water reactors, consists of various miscellaneous items, such as wood, cloth, plastics, filters, etc. Much of this waste is both compactible and combustible and can be properly incinerated.

It is difficult to estimate the quantities of medically generated LLRW. However, the U.S. Federal Drug Administration estimated that in 1981 there were more than 7 million radiopharmaceutical administered, 11 million nuclear medicine procedures performed, and 100 million radio-immunology procedures were performed as in-vitro diagnostic studies.[2] These wide spectrum of medical activities can produce LLRW in several physical forms (i.e., solid, liquid, or gas) as well as being chemical or biological in nature.[2]

Nuclear processing wastes such as halogenated solvents and cutting oils may be specifically listed RCRA hazardous wastes and may also be contaminated with low level radioactive compounds, such as the transuranic elements uranium and plutonium, at governmental atomic weapons plants and research laboratories. Such mixed LLRW can present special disposal problems and are often incinerated on site.

Radioactive Waste Classifications[16]

An important part of safe and efficient waste management is understanding the type and classification of low-level radioactive waste. The U.S. Nuclear Regulatory Commission divides low-level radioactive waste into 3 general classes-Class A, B, and C. Each class is based upon the concentration of radioactive materials and the regulatory requirements necessary to safely manage and dispose of waste products.

Class A Wastes are those which are relatively innocuous. Their waste packages are not required to maintain long term structural stability due to the low concentration of radionuclides, the low curie levels of the waste and the overall radioactive decay rates for the waste material. Examples include laboratory glassware, clothing, and biological wastes.

Class B Wastes are more radioactive than Class A wastes and require waste packaging in a structurally stable form. In general, the radioactivity will decay to levels that present an acceptable hazard to intruders within 100 years. Examples include radioactive medicines and tracers, and animal carcasses.

Class C Wastes are those wastes which will decay to safe levels within 500 years. These will have special disposal and packaging requirements and some form of barrier to reduce the potential of inadvertent intruders distrusting the waste packages. Examples include worn out reactor parts, used filters, most sludges.

LLRW Waste Management and Disposal

The waste management systems of today need to consider the best mix of these components: (1) Waste treatment, (2) waste transportation, and (3) waste disposal. There are few options for transportation other than truck and rail, with truck transport by far the most common mode. This along with limitations on quantity, or volume minimization requirements, have led many generators to consider waste treatment as one major option to be used at the source. Some states and compacts are considering waste treatment on a mass scale as a means to reduce the volume of waste to be handled in the disposal stage. The treatment alternatives available for consideration are:

(1) Source reduction: Efforts by generators to reduce volume and radioactivity by careful planning of operations, uses, and segregation of contaminated only materials.

(2) Storage for decay: Certain isotopes with fairly short half-lives can be stored for a period of time until they can be released as a non-radioactive waste.

(3) Compaction: This can effectively reduce void volumes in containers by a reduction in volume of 4:1. Presently available high force "supercompactors" that can compress compacted material further would only be cost effective at the regional site facility.

(4) Incineration: Provides the largest potential means of volume reduction, but depends on whether the type of waste generated is suitable for incineration.

(5) Solidification: Is a process used to provide physical stability to waste, such as liquid solidified by mixing with one of three media: cement, asphalt, or a polymer.

(6) Evaporation/Dewatering: Reduces the volume of evaporation and the mobility by encapsulation of the dried waste in a solid matrix such as cement, or one of the newer polymers.

In the past a certain amount of LLRW was packaged in 55 gallon steel drums, hardened with concrete, and dumped at preselected ocean sites. Today, most LLRW are disposed of by shallow land burial whereby such wastes are buried in excavated trenches, which are then backfilled with soil and capped.[1] Of the 6 commercial waste disposal sites, only 3 are currently operating and are in the States of South Carolina, Nevada, and Washington. Only certain U.S. government facilities, such as the U.S. Department of Energy, have onsite LLRW incineration facilities. Babcock & Wilcox is planning a commercial LLRW state-of-the-art facility in Apollo, Pennsylvania.

Much of the biomedical LLRW is incinerated onsite in largely poorly controlled existing hospital waste incinerators[3], as allowed by current U.S. Nuclear Regulatory Commission policies, if the radionuclides have been allowed to decay to background levels.

It is believed that most onsite and commercial hospital waste incinerators are not properly controlled by having high efficiency combustion plus an effective air pollution control (scrubbing) system[3]. Consequently, such improperly operated/uncontrolled hospital waste incinerators may emit significant emissions of toxic dioxins/furans, heavy metals, and possibly the potent carcinogen, BCME (bis chloro methyl ether) under conditions of poor incineration where significant aldehydes are present with HCl. This possibility of BCME forming from the reaction of formaldehyde and HCl has been reported in the literature, but has not yet been sampled for in biomedical waste incineration emissions.[5]

Compaction is another LLRW disposal technique which can accomplish significant waste volume reduction. However, when one compares the waste volume reduction factors of compaction with incineration, it is obvious that incineration offers much greater waste volume reduction for most LLRW categories.

Regulatory LLRW Perspectives

The federal LLRW policy act mandates are intended to provide disincentives that will encourage the states to develop their own permanent LLRW disposal facilities by 1993. The disincentives include increasing surcharges/ financial penalties and decreasing disposal volume allocations at existing disposal facilities located in Richland, Washington and Barnwell, South Carolina. If a state continues to be recalcitrant then the state must take title to all LLRW generated within its boundaries. These disincentives should force the states to more quickly toward compliance with the Act. New York State, for example, has adopted the NYS LLRW Management Act of 1986 to ensure that the state complies with such federal mandates by 1993.[4]

Radioactive and RCRA Emission Standards

For incineration of LLRW, the USEPA NESHAPS (National Emission Standards for Hazardous Air Pollutants) controls the emissions of radionuclides from U.S. Department of Energy and Nuclear Regulatory Commission (NRC) licensed facilities to 25 m rem/year dose equivalent to whole body or 75 m rem/year to critical organ. Doses due to Radon 220, 222 and their decay products are excluded.[6]

An alternative standard may be applied which ensures no exposure from all sources exceeding 100 m rem/year dose equivalent (continuous) or 500 m rem/year (non-continuous).[6]

Cancer risk assessments produced by the International Commission on Radiological Protection conclude that for uniform whole body radiation, the individual mortality risk factor for radiation induced cancers is about 5 x 10^{-5} for a 500 m rem dose.[6]

Mixed wastes are also controlled by USEPA RCRA 40CFR264 hazardous waste incineration standards that generally require 99.99% DRE (Destruction and Removal Efficiency) for POHCs (Principal Organic Hazardous Contaminants) 99% HCl (Hydrogen chloride) removal or 4 pounds per hour HCl emissions, and a total particulate emission of 0.08 gr/dscf corrected to 7% O^2.[6] This particulate emission standard is now considered obsolete and may be later revised by USEPA.[7] Other toxic emission standards may also apply to LLRW incinerators such as individual state and local standards for toxic contaminants, such as dioxins, furans and heavy metal emissions.

New biomedical waste incineration guidelines such as the recent draft Pennsylvania Department of Environmental Resources guides[14] specify a particulate emission concentration of 0.015 gr/dscf, (30 mg/dscm) 99.9% combustion efficiency and the above RCRA HCl emission controls.

State-of-the-Art Mixed Waste LLRW Incineration Technology

One of the longest operating, successful mixed waste LLRW incinerators is the Los Alamos, New Mexico controlled air incinerator for radioactive waste.[8] Figure 1 shows a process schematic of this LLRW incinerator, which began operating in 1973 and has been tested for weight and volume reduction with transuranic (uranium, plutonium content) wastes and LLRW since 1980. It has been fully operational since 1975 and has been permitted by USEPA to burn PCB wastes.[13] This modified 2 stage, commercial controlled air incinerator was initially tested burning suspect transuranic (TRU) waste consisting of room trash from the laboratory processing facility.[8] A total of 130 ft^3 of waste weighing about 470 lbs was incinerated initially to produce 1 ft^3 of ash weighing 16 lbs, resulting in weight and volume reductions of 29:1 and 130:1 respectively. Subsequent tests of TRU waste also gave similar volume reduction factors, because of the low density and high plastic content of the wastes. This incinerator was designed to burn wastes having a total 35% plastic content, of which 12% is PVC, plus 30% rubber.[8]

This modular, controlled air incinerator was also designed with special double-failure concept designs that include double seals, independent auxiliary supplies for most utilities, double check valves and auxiliary routing of liquid lines, and redundant pumps.

This controlled air incinerator has a 2 stage combustion design; consisting of a primary combustion chamber operated in a starved air mode at greater than 99.9% combustion efficiency, at nominal temperatures of about 1600°F in the primary, and 2000°F in the secondary combustion chamber.[9] It burns both solid

LLRW and has been modified to also directly burn halogenated solvents, oils, etc.[10]

The air cleaning system initially consisted of a water quench, high energy venturi scrubber, packed scrubber, off gas condenser/mist eliminator, reheater, and HEPA filter stages as shown in Figure 1.[8] In recent years, the air cleaning system was extensively modified to now include an activated carbon absorber followed by another HEPA filter,[10] as shown in Figure 2.[13]

The carbon absorber was installed in 1979 to control volatile radioactive contaminants, such as iodine, cobalt, cesium and iron-59.[10]

The incinerator scrubbing system uses a caustic scrubbing solution. The recycled scrubbing solution is filtered through filter cartridges which are later reburned in the incinerator. The scrubbing solution is automatically neutralized to a specific gravity of 1.05 or less to prevent excessive salt formation and clogging.[8]

Steam injection is used for liquid chlorinated wastes to minimize soot and to readily convert any residual chlorine gas to HCl.

The variety of process wastes burned in this incinerator are described in Volume I of report LA9427.[8] Nominally about 100 lbs/hr of mixed wastes are burned. However, a maximum of about 185 lbs/hr of solid and liquid wastes can be burned in this system.

In June, 1982 PCB tests were performed to demonstrate compliance with TSCA (USEPA Toxic Substances Control Act) which requires 1200°C, 2 second residence time waste incineration. 6-9's or 99.9999% destruction removal efficiency was demonstrated for PCB's in these tests.[10]

The above TSCA requirements were met burning a waste mixture of 60% Arochlor 1260 PCB, and 40% trichlorobenzene, at 25.4 - 43.4 kg/hr.[10]

Dioxin and furans were sampled for during these PCB trial burns in the incinerator off gases and before the carbon adsorber. However, USEPA laboratory consultants' dioxin/furan emission data for split samples, varied considerably, and was never officially accepted by USEPA as being valid or representative. There may have been problems in the analytical preparation of these split samples that gave varying PCDD/PCDF emission results, between these two analytical laboratories.[10]

Los Alamos Laboratory staff said that the specifications for the carbon bed adsorber were 99% or greater removal of methyl iodide.[10] Considering that high molecular weight substances such as PCDD/PCDF's have higher degrees of

adsorption and removal on activated carbon than methyl iodide, we could conservatively assume a minimum of 99.9% PCDD/PCDF removal efficiency in the carbon adsorber.

During September 1986, additional RCRA mixed waste tests were performed in this incinerator, burning about 185 lbs/hr of carbon tetrachloride, CC14, and trichloroethylene, TCE, adsorbed on Pellicil, a processed corncob adsorbent. Greater than 4-9's DRE, destruction and removal efficiency was demonstrated for CCl^4, and 6-9's DRE for TCE, as shown in Table I;[13] greater than 99% HCl removal was also demonstrated. Process CO, carbon monoxide emission concentrations were less than 20 ppm in all tests, indicating greater than 99.95% combustion efficiency.[10, 13]

The Los Alamos incinerator is one of the only operational LLRW incinerators that uses activated carbon adsorption following a two stage liquid scrubbing and HEPA filtration air cleaning system. Radioactive iodine isotopes are a major contaminant in biomedical LLRW and are very volatile. A control system design based on the control of radioactive iodine will also ensure the full control of dioxins, furans or transuranic metal halides such as uranium or plutonium halides, which may be of concern at other U.S. Department of Energy mixed waste/LLRW incineration facilities. Plutonium emissions are continuously monitored at the Los Alamos facility and have been negligible, proving the efficacy of this air pollution control system.[10]

The Mobile Volume Reduction System (MVRS) for LLRW[11]

In October 1981, the U.S. Nuclear Regulatory Commission established a policy encouraging the volume reduction of LLRW, and the need for waste generators to minimize the quantity of waste produced.

The Aerojet Energy Conversion Company's MVRS is designed for effective volume reduction of LLRW, and employs a controlled air incinerator with a liquid scrubbing off gas cleanup system and carbon adsorption to reduce waste volume for combustible low level dry solid radioactive waste and radioactive contaminated oil from nuclear power plants. It is also designed to process biomedical LLRW. Figure 3[11] shows a process schematic of the AECC MVRS.

The two stage controlled air incinerator consists of a primary combustor operating at negative pressure under starved air conditions at about 1600°F which is controlled by a supplemental fuel burner. The secondary combustion chamber operates at about 100% excess air and a high temperature of about 2100°F which is controlled by closed-loop modulation of the secondary air flow and by modulation of a second stage supplemental burner to provide complete combustion, i.e., 99.9% or greater combustion efficiency.

The incinerator is batch fed with compacted, shredded or non-compacted trash plus a small quantity of concentrated scrub liquor via an air lock and ram

feed arrangement. Contaminated oil is fed to the primary chamber by a separate burner or by incremental batch feeding along with the input trash. The total disposable materials are removed as ash from the primary chamber of the incinerator.

The off gas from the secondary combustion chamber is quenched and scrubbed of particulates and acid gases in dual caustic venturi scrubbers in series followed by HEPA filters and an activated carbon adsorber.[11]

The MVRS is mounted on three truck trailers; the trash preparation and ash handling trailer, the incineration trailer, and the off gas trailer.[11]

The AECC MVRS is capable of achieving an overall system decontamination factor of $4x10^6$ for particulate and 100 for iodine; thus expected annual releases, and plant site boundary concentrations of radionuclides are expected to be several orders of magnitude below federal limits.[11] Particulate emissions are designed to be controlled to an order of magnitude less than current USEPA RCRA emission standards.

The Savannah River Plant LLW Incinerator

Volume reduction of solid and liquid low-level waste has been demonstrated since January, 1985 at the Savannah River Plant (SRP) operated for the Department of Energy by the E.I. DuPont Company in South Carolina. LLRW is burned in the Waste Management Beta-Gamma Incinerator facility (BGI). The BGI utilizes a two-stage, controlled-air incinerator capable of processing 180 kg/hr (400 lbs/hr) of solid waste or 150 liters/hr (40 gal/hr) of liquid waste. These wastes are pyrolyzed in a starved, or substoichiometric air environment at 900 to 1100 degrees Celsius in the primary chamber are oxidized at 950 to 1150 degrees Celsius in the secondary chamber. A spray dryer, baghouse, and HEPA filter unit cool and filter the incinerator offgases.[14]

At the Savannah River Plant, about 70% of the solid waste contaminated with low levels of beta-gamma emitters is combustible. The waste is placed in 0.38, 0.53, or 0.61 meter cardboard boxes. All radioactive waste boxes that contain combustible waste and have suspect levels of contamination (<1 mR/hr @ 2.54 cm), are sent to the LLRW incinerator. This solid waste is composed of 63% polyvinyl chloride (PVC), 22% cellulosics, 10% polyethylene, and 5% rubber.[14]

For the past 30 years, spent solvent used in the Purex process for the radiochemical separation of plutonium and uranium has been stored at the SRP in underground tanks. The current generation rate is 7600 liters/year. Nearly 90% of this inventory of solvent has been incinerated to date. The liquid is composed of n-paraffin, a kerosene-like diluent, and 8-26% tributyl phosphate (TBP). The solvent is slightly radioactive, the principal beta-gamma nuclides being ruthenium, cesium, and strontium. Solvent cannot be incinerated if the

^{239}Pu concentration is greater than 0.001 g/gal or the ^{235}U concentration is greater than 0.013 g/gal, due to criticality concerns.[14]

A novel approach to incineration of phosphate wastes has been developed to facilitate operation of the BGI dry offgas system. Tetrabutyl titanate (TBT) is mixed with spent solvent prior to incineration. As the mixture is incinerated, the titanium reacts with the phosphorus to form a stable ash which can be readily removed in the baghouse. Without phosphorus fixation, a tar-like ash would form, which would adhere to and blind the baghouse filter bags. By using TBT, this effect has been greatly reduced, but not eliminated. A lime precoat applied to the filter bags prior to incinerating solvent has virtually eliminated baghouse pluggage.[14] New baghouse filter bags composed of 85% teflon and 15% fiberglass have been used to replace the previous fiberglass bags, which could not withstand the system's corrosive conditions and temperature fluctuations. The lime precoating is also expected to effectively neutralize acid gases from the burning of PVC and other chlorinated materials.

Processing steps in the Beta-Gamma Incinerator facility include solid and liquid preparation and feeding, incineration, offgas cleanup, semi-continuous ash removal and packaging, and radiation and contamination monitoring. Figure 4 shows a conceptual flowsheet of the incineration facility.[14]

LLRW Incineration in Japan

Low level radioactive waste incineration is widely used in Japan, especially for the disposal of LLRW from nuclear power plants. There are currently 14 LLRW incinerators in operation in Japan, and another 5 units are now under construction.[17]

The predominant type of incinerator used for burning LLRW in Japan is the NGK vertical, cylindrical combustion furnace, developed from the German KFK incineration technology.[18]

These Japanese incinerators are used to burn combustible radioactive wastes, including polyethylene sheets, bags, paper, wood, rubber,. waste oils, ion exchange resins, sludge and spent activated charcoal.[18]

The NGK LLRW incineration system is shown in Figure 5[18]. It has no grates or moving parts and operates as 800-1000°C without an external energy source after preheating. Waste lubricating oils are fired into the incinerator through a nozzle at the top of the incinerator. Spent resins and filter sludges dehydrated to about 50% water are fed to the incinerator by a screw feeder.[18]

The off gases from this incineration system first go to the primary ceramic filter, where entrained ash is filtered out, and volatile organics and soot are

combusted at 700-800°C. The gases then go to a secondary ceramic filter at 500-700°C. The filtered off gas is then air cooled to 250-300°C and then filtered through HEPA filters before being discharged to the atmosphere.[18] The NGK off gas treatment system has resulted in a radioactive decontamination effect of at least 10^5 at the outlet of the secondary filter, and at least 10^7 after the HEPA filter.[18]

The Japanese NGK LLRW incineration system appears to be highly effective for nuclear power plant LLRW. However it has no provisions for acid gas control, or for the control of trace, volatile, toxic compound emissions. The high efficiency dual caustic scrubber - HEPA filter-activated carbon adsorption off gas cleaning systems, for the Los Alamos and MVRS LLRW incinerators would be necessary for the burning of mixed wastes and biomedical LLRW with a significant halogen content.

New High Efficiency Multi-Stage Controlled Air Incineration Technology

Most controlled air incinerators used for LLRW incineration in the U.S. to date have been of the 2 stage combustion design. Newer, 3-4 stage controlled air incinerator designs seem quite promising for LLRW applications. This new waste incineration technology, shown in Figure 6, has been successfully used for incinerating biomedical and industrial wastes, and offers very high combustion efficiency operation with low oxides of nitrogen emissions, as a result of 3 or 4 stage burning with flue gas recirculation.

Control of Trace Toxic Emissions from LLRW Incineration

Testing at the Los Alamos incinerator and projections based on design calculations for the projected Babcock & Wilcox MVRS planned for Apollo, PA[11] indicate that such LLRW incineration facilities with multi-stage air cleaning can easily meet U.S. Nuclear Regulatory Commission and USEPA NESHAP radionuclide emission limits with a wide margin of safety.

Dioxin/Furan and Volatile Metal Halide Emissions

There has been much concern about dioxin/furan emissions by the public in the proposed Babcock & Wilcox MVRS Apollo, PA facility. There has also been concern about the possibility of trace volatile toxic metal halide emissions including uranium or plutonium halides from certain U.S. Department of Energy facilities, such as the Rocky Flats, Colorado mixed waste LLRW incinerator.[12] Such emissions are difficult to predict and to measure, but they can occur. Los Alamos Laboratory technical staff believe that the provision of activated carbon adsorption as a last air cleaning stage will properly control such emissions based on their continuous emission monitoring results for plutonium.[10]

We also know that dioxins and furans readily condense from the vapor state at temperatures less than 150°C,[15] onto fine particles. Such emissions would be readily condensed in a wet scrubber and totally collected by HEPA filters and activated carbon adsorption.

Heavy Metal Emissions

To date most evaluations of heavy metal emissions have concentrated on particulates. new models for heavy metals vaporization and condensation behavior indicate that we may be underestimating the release of metals as well as failing to remove them from the effluent stream.[15] Trichon and Feldman have studied the behavior of metals in flames, which indicate that due to a deficiency of oxygen in the center of the flame, metal oxides are reduced to suboxides or pure metals which may then vaporize and remain in the emissions as vapors or fumes.[15] Metals may further react with acid gases to form chlorides, or with other waste products to form carbonyls, which readily vaporize at high temperatures.[15]

For example, chromium carbonyl could form in the carbon monoxide rich flame interior and vaporize in the incinerator. Theory predicts that lead, lead oxide and lead chloride will all vaporize at fairly high rates. Lead chloride vaporizes most rapidly at low temperatures, and lead and lead oxide vaporize at almost the same rate at expected incinerator operating temperatures between 727 and 827°C.[15] Thus lead and its compounds will vaporize within the reducing flame interior and in the oxidizing part of the incinerator combustion chamber.[15]

Many types of metals can be present in LLRW, in both biological and non biological wastes. Radioactive metal isotypes with short half lives may be depleted prior to incineration, however they may still cause toxic heavy metal emissions when incinerated if not properly controlled. The combination of gas scrubbing, significant temperature reduction, HEPA filtration, and activated carbon adsorption, as in the case of the Los Alamos waste incinerator, is expected to fully control such emissions.

The proposed Babcock & Wilcox MVRS LLRW incineration system's carbon adsorption system is designed to primarily control trace radioactive iodine which is the most volatile and difficult contaminant to control. If radioactive iodine, I_2 is controlled to a high degree, then the volatile metal halides, dioxins and furans will also be controlled to a very high degree, at projected non-detectable levels.

Conclusions

Low level radioactive wastes are increasing in our society. The limited number of commercial LLRW disposal facilities is forcing several states to develop their own local disposal sites.

Many public officials and the public are not yet aware of state-of-the-art incineration technology for LLRW, using for example, high efficiency controlled air incineration, and multi-stage, state-of-the-art air cleaning technology. We must educate them, and demonstrate that LLRW incineration can be the best and safest method to properly dispose of such wastes; in conjunction with proper containment and disposal of LLRW incinerator ash.

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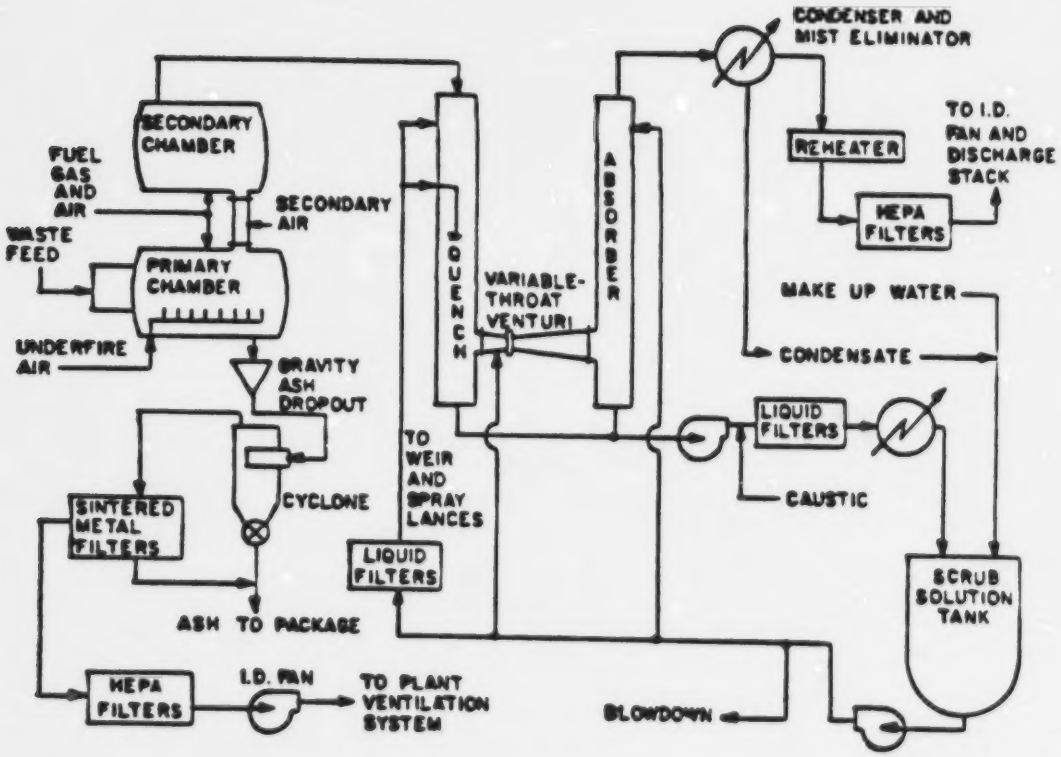
FIGURE 1

LOS ALAMOS TRANSURANIC WASTE INCINERATOR



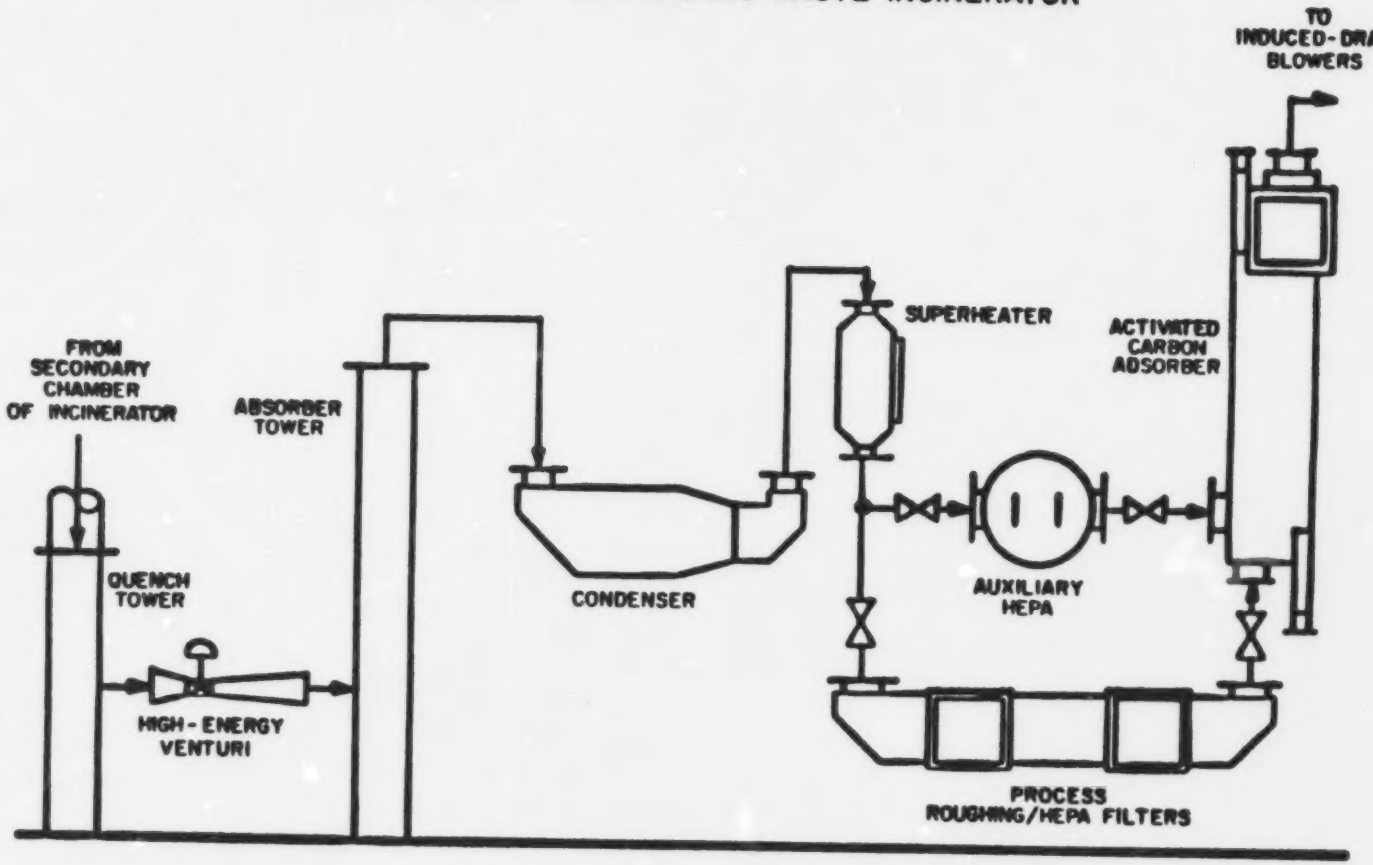


Fig. 2. OFFGAS CLEANING SYSTEM

Table I

USEPA RCRA TRIAL BURNS
FOR THE LOS ALAMOS, NEW MEXICO
TRANSURANIC WASTE INCINERATOR[13]
CONDITION 4
SOLID FEED
2000°

RUN NUMBER	1	2	3	4	5	6
Secondary Chamber Temperature, °F	2000					
CCl_4 Feed Rate, Lb/hr	57	57	59	59	62	62
TCE Feed Rate, Lb/hr	28	28	28	28	30	30
EXHAUST FLOW RATE, Lb/hr	3690	3690	3890	3890	3930	3930
CCl_4 DRE, %	99.99848	99.99983	99.99922	99.99824	99.99839	99.99865
TCE DRE, %	99.99997	99.99999	99.99998	99.99985	99.99991	99.99993

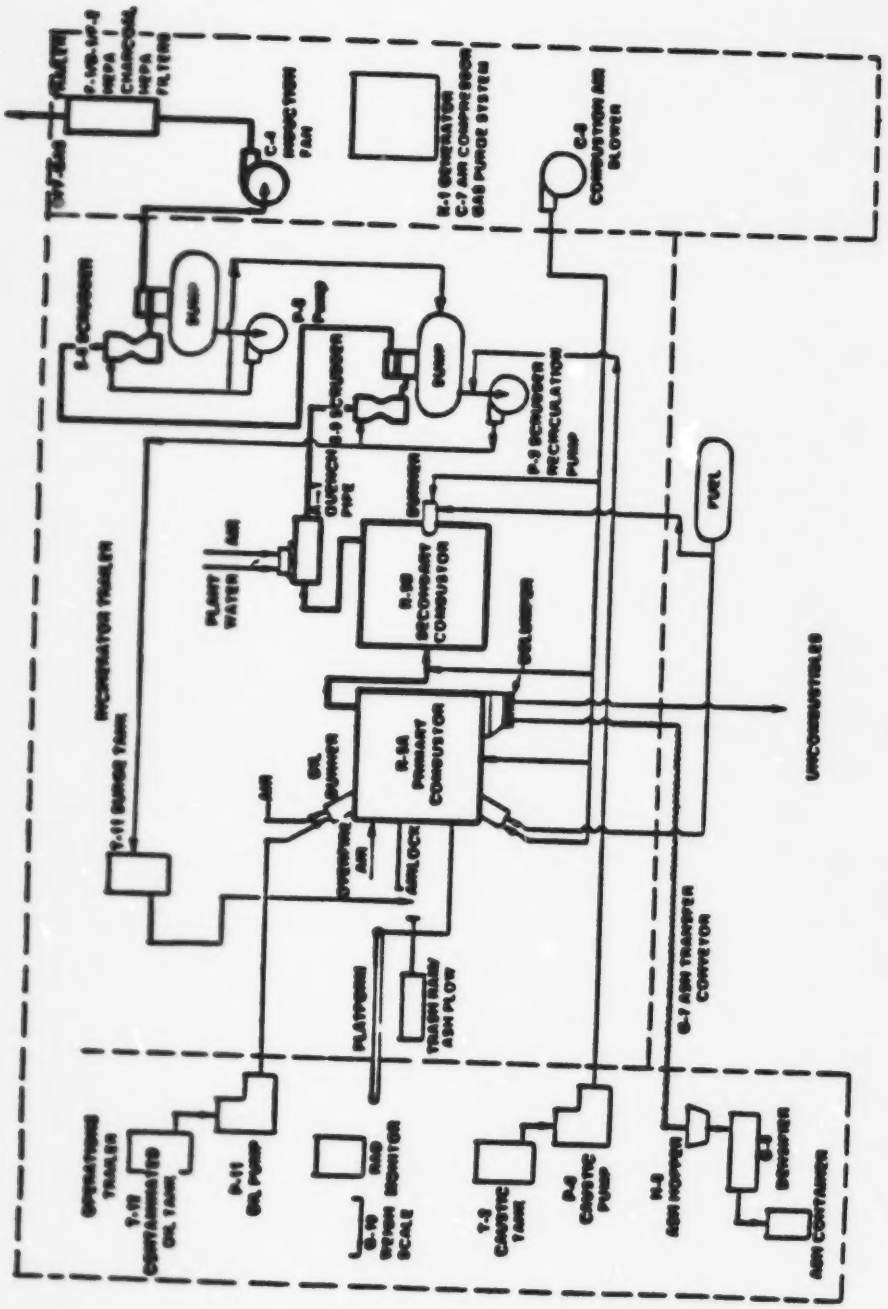


Figure 3. AECC Mobile Volume Reduction System Schematic

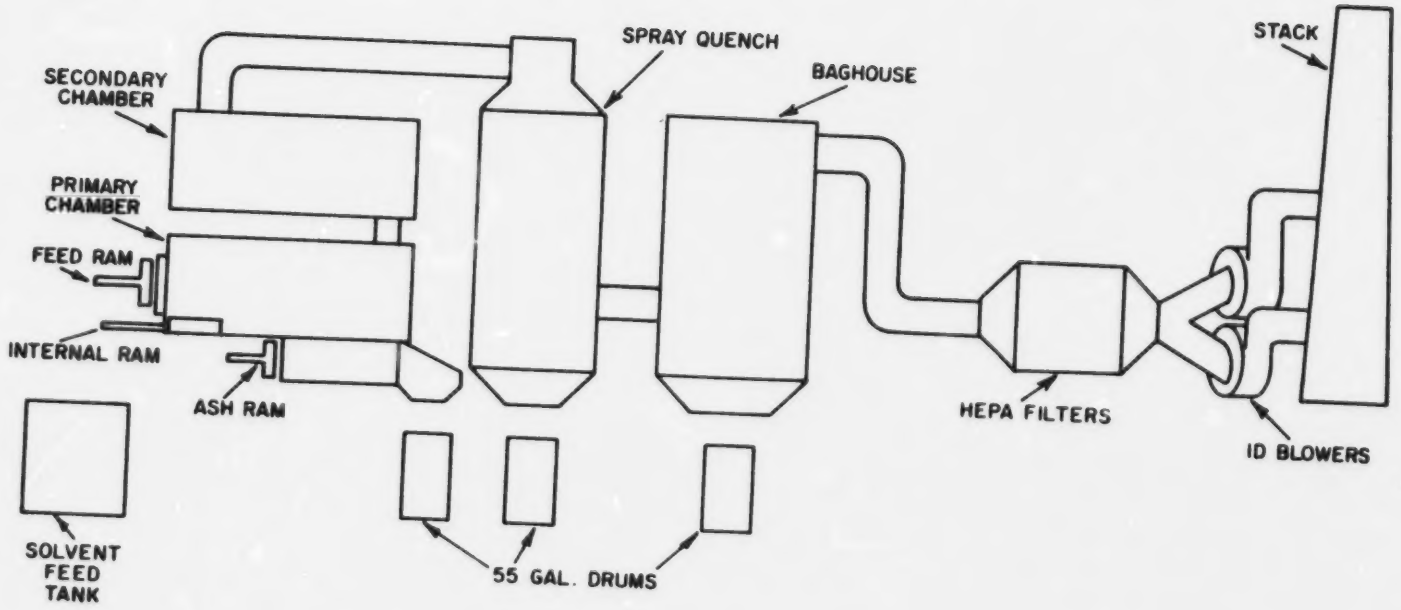


FIGURE 4. PROCESS FLOWSHEET
SAVANNAH RIVER LLRW INCINERATION SYSTEM

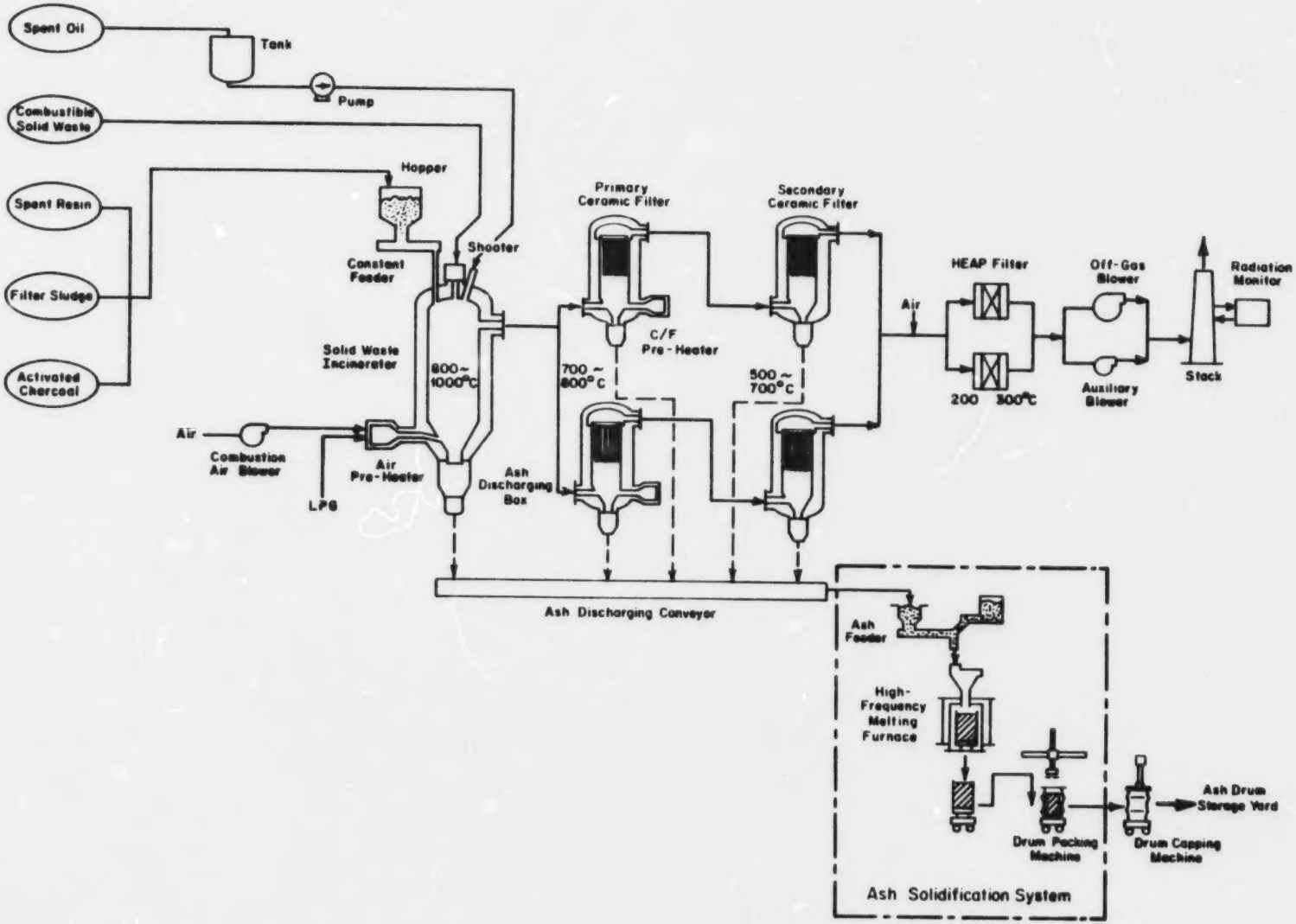
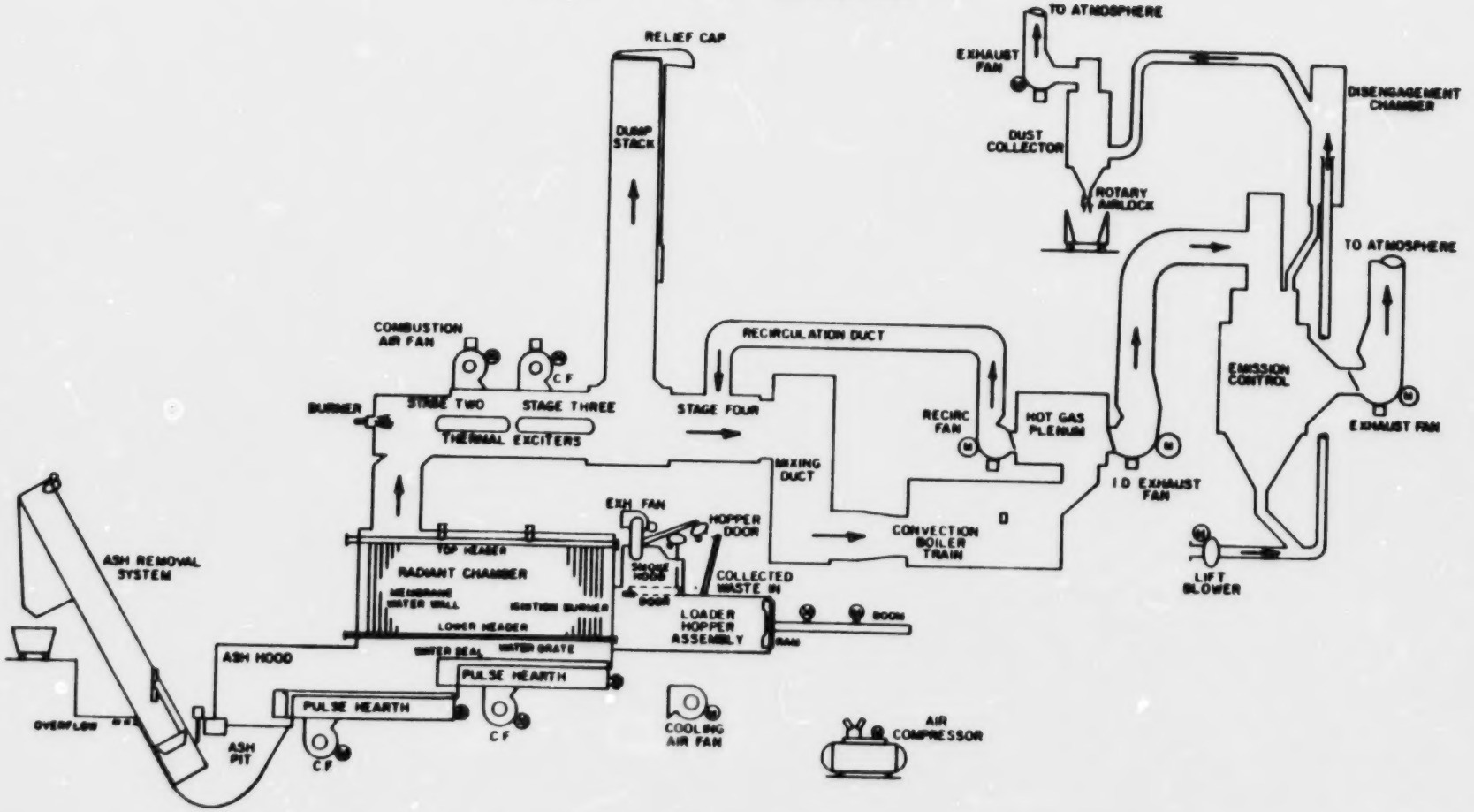


Fig. 5. PROCESS FLOW CHART OF NGK COMBUSTIBLE LOW LEVEL RADIOACTIVE WASTE INCINERATION SYSTEM.

Figure 6

MODERN CONTROLLED AIR WASTE INCINERATOR
THREE STAGE + COMBUSTION



Courtesy: BASIC ENVIRONMENTAL ENGINEERING, INC

TENDANCE ACTUELLE EN SANTÉ ENVIRONNEMENTALE ET DU TRAVAIL

Par

Dr. Albert Nantel
Centre hospitalier de l'Université Laval

Article non disponible au moment de l'impression

A COMPARISON OF RISK ASSESSMENTS OF TRIS (2,3-DIBROMOPROPYL) PHOSPHATE

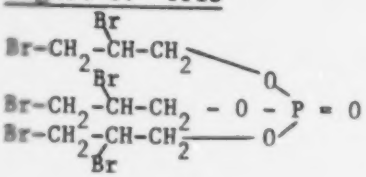
John C. Bailar III
Department of Epidemiology and Biostatistics
McGill University School of Medicine

BACKGROUND

Tris-(2,3-dibromopropyl) phosphate (Figure 1), commonly called Tris, has had several important uses, including use from 1972 until early 1977 as a flame retardant in polyester, acetate, and triacetate fabrics and clothing.

Figure 1: Tris

Chemical structure:



Molecular formula: $(BrCH_2BrCHCH_2O)_3PO$

In 1977, imminent regulatory action by the Consumer Product Safety Commission (CPSC) persuaded garment and textile manufacturers to stop using Tris on clothing and on fabric meant for clothing. This case study examines and compares the health risk assessments that led to that action, particularly assessments of the risk of using Tris in children's sleepwear.

Because of concerns about cancer, CPSC investigated and eventually regulated Tris under the Federal Hazardous Substances Act (FHSA, Section 2(q)(1)(B)), which gave it authority". . . to investigate risks of injury associated with consumer products and to regulate products to reduce or eliminate certain risks of injury associated with them. Such orders may take the form of bans of the sale of products in interstate commerce and repurchase of those products . . ."

Five risk assessments were used in the regulatory decision-making process of the CPSC. The industry voluntarily stopped using Tris on garments at about the same time the CPSC was considering action, so in practical terms the issue was whether to ban the sale of the existing stock of garments, fabrics, and yarn and to require manufacturers to repurchase Tris-treated items. The CPSC determined that children's wearing apparel and certain Tris-treated uncut fabric, intended for sale to consumers to use in such apparel, were hazardous substances within the meaning of the HSCA. CPSC banned their sale on or after April 8, 1977, and ordered that Tris-treated apparel and fabric sold to consumers before April 8 but not yet washed was to be repurchased.

The principal concern was that Tris was mutagenic and carcinogenic. A mutagenic hazard was first identified by Ames in a S. typhimurium assay (Prival et al., 1977), and a National Cancer Institute (NCI) bioassay of Tris in feed established a risk of renal and other cancers in rats and mice. The NCI study was completed in 1978 (NCI,1978), but preliminary results were reported to CPSC in 1977.

The five risk assessments examined the carcinogenic effects of Tris. The Environmental Defense Fund included a risk assessment in its petition to CPSC to regulate or ban Tris; CPSC included a risk assessment in its

Federal Register notice that did ban Tris-treated fabric and apparel; and other risk assessments were conducted by NCI staff, the Bureau of Biomedical Science (BBS) of CPSC, and Hooper and Ames. All of the risk assessments were done within a period of about six weeks, and all used or had access to much the same data.

REVIEW OF THE RISK ASSESSMENTS

History

It was just over one year from Ames' first report on the mutagenicity of Tris (January 1976) until CPSC banned Tris-treated children's clothing from commerce (April 1977). However, the regulatory chronology begins in 1971, when the Federal Trade Commission (FTC) required that children's sleepwear meet minimum flammability standards.

From the summer of 1972 to early 1977, Tris was used as a flame retardant in wearing apparel, particularly polyester, triacetate, and acetate children's sleepwear garments. Some of the Tris was available on the surface of the garments, and might be absorbed through skin or ingested when children mouthed the garments. The Bureau of Environmental Sciences (BES, 3/15/87) of CPSC reported that Tris was applied internally to acetate and triacetate fibers, and externally to polyester fabrics. Acetate fabrics contained 65 to 600 ppm surface Tris, while polyester fabrics contained 260 to 37,500 ppm. Laundering removed much but not all of this surface Tris. Morrow found that 3 washings decreased the available Tris on polyester from 4,330 ppm to 65 ppm; on acetate it decreased from 600 to 90 ppm, and then apparently remained at 90.

When the FTC set flammability standards for children's sleepwear, scientists at NCI knew that Tris might be used as a flame retardant, and that it had not been tested for carcinogenicity. Because it was a halogenated hydrocarbon, it was suspect as an alkylating agent and a carcinogen. Because it was an organophosphate, there was concern that it might be absorbed. And because of the amount of Tris in children's sleepwear, up to 15 percent by weight before 1975, exposure might be high. After a preliminary skin painting study to establish toxicities and appropriate doses, Tris was included in the NCI bioassay program.

In January, 1976 Ames (Ames, 1976) brought Tris to the formal attention of CPSC in a letter that expressed concern about the mutagenic and carcinogenic potential of Tris, and cited his findings that Tris induced mutations in Salmonella typhimurium, both in the presence and in the absence of metabolic activating systems. EDF petitioned CPSC In March, 1976 to require warning labels on Tris-treated garments because of the results of these mutagencity tests and because of the chemical similarity between Tris and some carcinogenic organophosphates.

Principal Information Available for Risk Assessments

The risk assessments of Tris relied largely on the NCI bioassay data; on a few measurements of the availability of Tris on the surface of garment by the Dupont and Michigan Chemical companies; and on data from Michigan Chemical regarding the absorption of Tris through the skin or by mouthing of garments. Ames and Prival provided data on the mutagenicity of Tris.

The NCI bioassay was central to the risk assessments. Groups of

approximately 50 weanling rats and 50 weanling mice of each sex were kept on diets with Tris at levels of 0, 500, or 1,000 ppm (mice) or 0, 50, or 100 ppm (rats). Animals that died were examined for pathologic changes, and after two years all surviving animals were killed and similarly examined. Table 1 shows the organs with significant increases in tumors. Mice developed dose-related increases in cancers of the kidney, stomach, liver, and lung, whereas rats, treated at 1/10 the doses in mice, showed an even larger increase in kidney cancers, but no statistically significant increase in other tumors.

TABLE 1

NUMBERS OF ANIMALS WITH TUMORS/NUMBERS EXAMINED

Tris Dose Level (ppm in diet)	KIDNEY M	KIDNEY F	STOMACH M	STOMACH F	LIVER M	LIVER F	LUNG M	LUNG F
				MICE				
0	0/55	0/55	0/51	2/52	28/55	11/54	12/55	4/55
500	4/50	2/50	10/48	14/48	30/49	23/49	18/44	9/50
1,000	14/50	2/50	13/50	22/49	23/50	33/50	24/50	17/50
				RATS				
0	0/54	0/54						
50	25/55	4/55						
100	29/55	10/55						

M,F = male, female
Source: Brown, Schneiderman, Chu. March 1977, p.1.

National Cancer Institute (NCI) Assessment of Tris

This risk assessment, referred to as Schneiderman's, was prepared by Brown, Schneiderman, and Chu (1977) at the request of CPSC.

Hazard Identification The hazard was identified from the NCI bioassay, in which Tris ingestion was associated with increased cancer of the kidney, stomach, liver, and lung of mice, and of the kidney of rats.

Hazard characterization Two critical methodological choices affecting hazard characterization, and thus the shape of the dose/response curve, are scaling factors and dose-response models. NCI converted animal doses, initially measured in ppm in the daily diet, to mg/kg/day. NCI then used a surface area model to convert these levels to comparable human exposures using the formula:

$$d_B = d_A / (W_B/W_A)^{2/3},$$

where A and B are the two species (rodents and humans in this case); d = dose; and W = weight. This method permits risk assessments for children of different sizes; Schneiderman used weights of 10 and 20 kg.

Exposure characterization Schneiderman used Harris' exposure estimates, which were based in part on information obtained from Michigan Chemical Corporation. The estimates ranged from 0.085 to 85.0 mg/kg total lifetime exposure, depending on the number of Tris-treated garments worn by the child and on whether exposure was by mouthing the garment or from skin absorption (Table 2). He did not include a factor for the dependence of in absorption on the amount of skin exposed and therefore on the size of the child.

Table 2
Harris' exposure estimates

Exposure Assumption	Resulting Exposure to Tris (mg/kg/lifetime)
1 garment: mouthing only	0.085
10 garments: mouthing only	.85
1 garment: skin absorption	8.5
20 garments: skin absorption	85.0

Risk determination Schneiderman used two different dose-response models: the single-hit model, and the log-probit model with an assumed slope of one. The single-hit model is approximately linear at low doses, and Schneiderman stated that it provided a conservative estimate of risk at low doses. He commented that the use of other models would not have produced significantly different results, and noted that although the data fit the models, there was no way to know whether either model was correct at very low doses. He estimated the lifetime risk of tumors for each exposure level from data for each tumor site in each sex and species, expressed as the 95% and the 99% upper bounds on the maximum likelihood estimate (MLE). The MLE was described as the "best" estimate of the number of children that will get cancer, and the upper bounds are values that would be higher than the true (but unknown) value in 95% or 99% of such estimates, given that the underlying model is correct. Schneiderman discussed briefly whether and how to combine data for tumors at different sites, and stressed the need for caution because little is known about competing risks, differing rates of spontaneous cancer, and whether the risk of getting cancer at one site is independent of the risk at other sites. He suggested that the risks estimated for each site using the single-hit model might be added to arrive at an estimate of the overall carcinogenic hazard.

In a hearing before the Commission, Schneiderman presented his written risk assessment and explained the basis, use, and limits of extrapolation models. Both presentations were at the level of technical expertise of the Commission members and set in a framework of helpfulness rather than a defense of a formula or formal procedure for risk assessment.

A cover letter (Schacter, 1977) summarized the risk assessment as predicting a lifetime risk of kidney tumors of 52 per million, based on data from mice and a lifetime exposure of 85 mg/kg. Estimates based on the rat data would be 40 times higher, or about 2080 per million.

Environmental Defense Fund Assessment of Tris

Harris of the Environmental Defense Fund (EDF) presented three sets of estimates of risk: rates (individual probabilities of cancer) based on daily exposure levels, rates (ten times higher) based on total lifetime exposure, and numbers of cases projected from exposure of three million infants per year.

Hazard identification Harris identified Tris as an animal carcinogen and a potential human carcinogen because it caused tumors at multiple sites in two species in the NCI bioassay. Harris argued in a meeting with the CPSC Commissioners (3/8/77) that Tris was a potent carcinogen because the NCI bioassay showed that relatively low doses caused cancer at numerous sites.

Hazard characterization Harris maintained that current theories of carcinogenesis as well as the differences between children and laboratory animals in the dose and duration of exposure supported his use of risk estimates based on straight line (one-hit) methods and total accumulated exposure. Although the bioassay suggested that cancer rates in rats were at or near a plateau between 50 and 100 ppm, and although the Mantel/Bryan (probit) model approaches a plateau at very high and very low doses, Harris explained that it was not as good as the single-hit model. This was because other carcinogens in the environment essentially "use up" the flat part of the Mantle/Bryan curve at low doses, and new exposures start from a part of the curve that is closer to a straight line. Harris emphasized that there is no "correct" way to extrapolate from high to low doses or from animals to humans, and noted that there was considerable controversy in the field.

He also noted that the NCI bioassay did not account for two factors that might increase the carcinogenic potential of Tris: (1) possible synergy with other environmental contaminants; and (2) the age of humans exposed to Tris-treated garments. Animals in the bioassay were adults or near adults, and much data suggest that newborn and very young offspring (both rodents and humans) are more susceptible to some carcinogens than adults. Also, children, unlike the experimental animals, would have their entire exposure to Tris during early life, and there was no generally-accepted procedure to account for short-term versus long-term exposure, or for early versus lifetime exposure. Harris did not adjust his estimates for these factors, and noted that his figures may therefore underestimate the actual risk.

He presented two sets of calculations. One used the single-hit model and the same dose calculations as Schneiderman; this produced risk estimates essentially the same as Schneiderman's. The other used the conclusion of a 1975 National Academy of Sciences (NAS) report (Pest Control, referenced in Harris, p. 10) that estimates of lifetime cancer risk can be based on total lifetime dose per unit body weight, rather than on the daily dose rate. Harris found that a lifetime accumulated dose of 1,825 mg/kg (2.5 x 730 days) caused kidney tumors in 45 percent of rats (the most sensitive species), and estimated that a similar lifetime dose in humans would cause a similar rate of cancer. These estimates were approximately 10 times higher than those obtained from a calculation based on mg/kg/day or on the daily dose rate.

Exposure characterization Harris, like Schneiderman, based his exposure estimates (Table 2) on work by Blum and Ames. He stated that tests conducted by the Dupont Chemical Company found skin absorption as

great as that estimated by Blum and Ames (3/28 meeting). Table 3 presents Harris's estimates using the Mantel/Bryan model, the single hit model, and the NAS method.

TABLE 4

EXPOSURES TO TRIS-TREATED GARMENTS AND RELATED CANCER RISK

EXPOSURE SCENARIO	EXPOSURE IN MG/KG OF CHILD AGED 0-1 YEAR	EXPECTED CANCER CASES, ASSUMING THREE MILLION EXPOSED INFANTS		
		Mantel/Bryan	Single hit	NAS Method
1 garment (mouthing only) (Michigan Chemical)	0.085	.3	7	63
10 garments (mouthing only) (Michigan Chemical)	0.85	14	69	630
1 garment (skin absorption) (Ames & Mybach)	8.5	1,170	690	6,300
20 garments (skin absorption) (Ames)	85.0	28,800	7,500	63,000

Source: Harris Risk Assessment

He also used the estimate of Michigan Chemical that an infant under age 1 wearing one set of sleepwear receives .85 mg/kg from mouthing, in addition to exposure from skin absorption. EDF argued to the Commissioners that, even without proof of skin absorption, the data were strong enough for the Commission to act (3/28 meeting).

Risk determination In their summary requesting regulatory action by CPSC, EDF stated that the risk of allowing the current stock of Tris-treated garments to be sold for one more year was somewhere between 7 and 6,300 cancers. Harris' document did not quantify this uncertainty, but his oral presentation to the Commissioners gave ranges of expected cases at each exposure level.

Hooper and Ames Assessment of Tris

Hooper and Ames, who did the early in vitro work on Tris, submitted a risk assessment to CPSC and urged that Tris be removed from the marketplace.

Hazard identification Hooper and Ames identified Tris as a Salmonella mutagen from tests with both human and rat liver activation.

Tris also caused large numbers of recessive lethal mutations in the offspring of Drosophila (fruit flies), damaged human DNA in in vitro experiments, and caused unscheduled DNA synthesis in human cells in tissue culture. Dibromopropanol, a metabolite of Tris, was also a mutagen.

Hooper and Ames also identified Tris as a likely human carcinogen on the basis of the NCI bioassay results and because of the results of the short-term tests on human tissue described above. They were especially concerned because of the chemical's contact with the scrotum, through which absorption of similar chemicals is especially rapid and complete (Hooper and Ames, 1977), and because absorption seems to be increased in the presence of urine.

Hazard characterization Hooper and Ames used much the same lifetime cumulative dose as did Harris for extrapolating from rats to humans. They claimed that the dose that children would receive (70 mg/kg/year) was so close to that received by the rats that the choice of mathematical model was unimportant.

Exposure characterization Hooper and Ames estimated exposure to Tris from the following information and assumptions:

- Twelve Tris-treated garments would be worn during the first year of life (based on industry sales data).
- Each garment had 5,000 cm^2 of surface area, 2,500 of which would be in contact with the child at any one time.
- It was sufficient to consider polyester because most sleepwear was made from polyester. They calculated the amount of Tris available for absorption per cm^2 from the amount removable from fabric with solvents, using a number halfway betwen the amount of Tris available on "high" and "low" surface Tris garments, adjusted for washing garments after each wearing; garments washed 50 times a year. They calculated that 30 mg/cm^2 of Tris was available for absorption.
- From work by Morrow et al. on skin sensitization by Tris and work on absorption of related chemicals, they estimated that 6 percent of available Tris would be absorbed through the skin and that 1 percent of that amount would be absorbed through mouthing of garments.
- They estimated from the 30 mg/cm^2 of "surface" Tris available that a child aborbs .54 ug/cm^2 each day x 2500 cm^2, or 70 mg/kg/year (0.54 ug/cm^2 Tris x 2,500 cm^2 = 1,350 ug/child/day x 365 days ÷ 7 kg/child = 70 mg of Tris absorbed/kg/year).

Risk determination Hooper and Ames simply multipled the 45% incidence of kidney tumors in male rats treated at 50 ppm by 70/1825, where 70 mg/kg is the amount of Tris a child is exposed to in one year and 1825 mg/kg is the lifetime exposure of the rats at 50 ppm in the diet. This corresponds to a 1.7% lifetime incidence rate in children, or 63,000 cancers year for each 3 million exposed infants (Table 3). Hooper and Ames did not attach statistical descriptors such as upper bounds or maximum likelihood estimates, but emphasized that the risk was unacceptably high even if it was off by a factor of 10, and that

immediate action was necessary to eliminate exposure. Their estimate of risk is three times higher than the highest risk in any of the other risk assessments because of the mathematical model they used and because the assumed exposure is close to the highest level of exposure used in the other risk assessments.

Consumer Product Safety Commission's (CPSC) Two Assessments of Tris

CPSC could not regulate Tris unless it reached a formal determination that Tris was a hazardous substance within the meaning of the FHSA, and that children's garments containing Tris were a bannable product. Once CPSC received the EDF petition, it moved very quickly to collect data on the hazards of Tris, on exposure, and on the market.

The Commission was working under severe time constraints and a great deal of public pressue and publicity, including four Congressional hearings on Tris during the short time that CPSC considered the EDF petition. CPSC produced an initial risk assessment (Bayard, 1977) and a somewhat more detailed risk assessment (April 8 Federal Register, slightly extended in June 1 Federal Register) banning children's clothing and other items treated with Tris. Except where noted, the following discussion describes the risk assessment in the Federal Register.

Hazard identification CPSC cited the NCI bioassay as evidence of animal carcinogenicity. It referred to Schneiderman's testimony, the EDF petition, the CPSC medical director, Hooper and Ames, and the National Cancer Advisory Board to support the idea that, in the absence of human data, animal carcinogens should be considered potential human carcinogens. Commission staff also stated (CPSC and EDF) that short-term tests were not sufficient to establish carcinogenicity.

Hazard characterization CPSC considered its risk assessment quite important, since Tris was one of the first chemicals to come through its bioassay program. Also, the risk assessment of Tris was the first in which CPSC had to rely solely on animal data. Thus, the problem with Tris was compounded by the need to develop new policies on how to use animal data to assess human risks. CPSC staff did not know whether the Commission would act on animal data alone or require demonstrated cause and effect in human beings, and recognized that the decision on Tris might be a precedent for other animal carcinogens for which there were few or no human data.

CPSC used much the same methods and asumptions as Schneiderman: animal doses can be converted to equivalent human exposure levels; animals and man have equal sensitivity to Tris at equal converted levels; infants and children are not more or less sensitive than adults; and the dose given to an animal during its entire life can be converted to an equivalent daily dose for some period that is less than a lifetime. The BBS concluded that the kidney is the primary target organ of Tris, and estimated the risks of Tris from data on kidney tumors in male rats, the most sensitive sex and species tested.

CPSC staff discussed the existence of a threshold (safe) level with Harris, who contended that there was no safe level. At least one of the Commissioners stated in a meeting with EDF that he believed that a substance found carcinogenic in animals must be assumed to be carcinogenic to humans, and, since it is not possible to determine a safe level of exposure to a carcinogen, that ". . . whenever possible no exposure should be permitted." (p. 23, 3/8/77 meeting)

Exposure characterization Estimates for exposure to Tris ranged more widely than estimates of any of the other variables in the risk determination. While many questions were directed at the amount or proportion of Tris absorbed, a basic concern was whether the experiments reliably indicated that any was absorbed. As one Commissioner said, "The question for me is whether this product Tris is getting in the system at all. And I think the tests . . . indicate that it is. . . . If those studies do support the contention that it is getting into the system, the fact that the number is off by two or five or ten doesn't impress me too much" (transcript, 3/8/77 hearing). In April 1977, BBS did its own radiolabeling tests for dermal absorption and showed clearly that Tris was absorbed in rabbits and rats (BBS/CPSC, 4/1/77). Absorption was enhanced by the presence of urine in the cloth and depended on the body area exposed to the Tris-treated garments. BBS estimated from these dermal tests of rats and rabbits that a child might absorb from 2.5 to 77.4 mg/kg of Tris (BBS, 4/1/77).

Risk determination The BBS risk assessment was based on its own exposure estimates, the NCI bioassay data, Schneiderman's methods for dose extrapolation, and the mathematical models he described. The BBS "best" estimate (MLE) was approximately 300 kidney cancers per million male exposed. BBS estimated the lifetime risk of kidney cancer to be between 60 and 1,800 per million exposed males using the single-hit model, or 25 to 5,100 cases using the log probit model. It is not clear whether these lifetime risk estimates were best estimates or 95 percent confidence limits. CPSC also quoted rates for females. The range among these many sets of numbers did provide some indication of uncertainty of the estimates.

CPSC discussed the effect of washing Tris-treated garments, commenting that 85 to 95 percent of surface Tris was removed by three washings of polyester fiber. The Commission also noted that Tris was not essential for manufacturers to meet the nonflammability standards for children's sleepwear.

CPSC felt that it had to meet a stricter burden of proof and demonstrate a higher level of risk to recall merchandise than to simply ban future use of Tris. CPSC was also concerned that the data and the risk estimate be strong enough to withstand a court challenge.

The Commissioners discussed with EDF that the estimates were all very uncertain and that the lowest estimate (.3 cancers for one additional year of exposure), based on the least conservative mathematical model (Mantel/Bryan) and the lowest exposure (mouthing one garment), was not "impressive" (p. 3, 3/8/77). EDF responded that this estimate was unreasonably low because the mathematical model was not appropriate for extrapolation to low doses; the exposure level was unlikely because a child would have more than one set of sleepwear in the first year; infants were probably more susceptible to carcinogens than adults; and regulation even at the lowest estimated level of risk had been carried out by other agencies and would withstand a court challenge.

CROSS-AGENCY ANALYSIS

The risk assessments are quite similar in their approach, perhaps reflecting the high degree of cooperation among the parties. The most important similarities were:

- They all assessed the risk of cancer.
- They all relied on the same exposure data and the same NCI bioassay.
- They characterized the risk similarly: They relied on the incidence of kidney tumors; they assumed equal susceptibility of animals and humans; they expressed dose as mg/kg/Body weight.

In addition, EDF, Schneiderman, and CPSC calculated estimates of risk using the same set of mathematical models to extrapolate from high to low doses. However, they did not agree about which of these models was most appropriate.

The most significant differences among the risk assessments were in the ways they estimated human exposure and in their choices of dose-response models.

Estimating Human Exposure

Quantifying human exposure seemed the most difficult part of the risk assessment, though there was no doubt that exposure occurred once results of the radiolabeling studies were available. The questions concerned how to convert animal exposure to human exposure; whether Tris was absorbed through the skin; and, if so, how much. Estimates of the amount absorbed depended on the availability of Tris from new and washed garments and on assumptions about how many Tris-treated garments a child would wear.

Two basic approaches were used to convert animal exposure to human exposure. Harris and Ames used cumulative lifetime dose, which increased estimated risks by an order of magnitude at each exposure level over the estimates made by Schneiderman and CPSC. Harris and Ames believed that a cumulative lifetime dose compensated for differences in the exposure patterns of humans and experimental animals. Humans were dosed as infants and received their total dose early in life, which they claimed would make the dose more effective than if it were administered from early adulthood until death, as was the case with the animals. They cited evidence that children, and particularly infants, are more susceptible to carcinogens than adults. In addition, the long latency period of cancer may cause doses given early in life to be more carcinogenic than doses given later and/or shortly before effects could be measured. Schneiderman and CPSC converted lifetime animal doses to equivalent daily doses over less than a lifetime.

There was much discussion of exposure, among the Commissioners and between EDF and the Commissioners, to establish the fact that Tris was, in some amount, absorbed through the skin. By the end of this discussion, the radiolabeling experiment appeared to leave no doubt that Tris could be absorbed. Futhermore, Morrow had found that sensitized subjects would react to patches of fabric that contained Tris, showing that the material penetrated the skin.

The discussion then shifted to how much Tris was absorbed through the skin. Estimates differed by three orders of magnitude. These differences were based on different assumptions about the number of garments that a child would wear and on different calculations of the

amount of Tris absorbed from any one garment. Although Hooper and Ames produced the exposure estimates that were used in all of the risk assessments, Ames estimated the risk of cancer at only the highest estimated exposure. The other risk assessments presented risks at each order of magnitude.

Basis for Calculating Risk

Another difference in the risk assessments is that Schneiderman looked at kidney tumors in both mice and rats, while the other risk assessments concentrated on data from male rats only. Bayard (BBS) provided risk estimates for females as well as males. No other risk assessment mentioned rates for females in the text, although this information was included in charts by Harris and Schneiderman.

Other issues that were discussed at least briefly in the risk assessments included synergy, age at exposure, and duration of exposure. Synergy was mentioned as likely to be present in the real world; as a reason for using a linear model for extrapolation to low doses; and (by Ames and by EDF) as a reason for thinking that current methods of estimating risk were likely to underestimate risk. Each report mentioned the likelihood that early exposure causes more cancer than later exposure and that infants would be more susceptible to carcinogens than adults. This information was not used directly in the calculations, but it was used to justify the use of cumulative lifetime exposure and linear dose/response extrapolations.

Different statistics were presented to describe the estimated risk. CPSC and Harris used upper confidence limits (UCLs). Schneiderman depended on maximum likelihood estimates (MLEs), although he also provided UCLs. He apparently chose the MLE because he believed it was the "best estimate" of risk. Only Schneiderman (a statistician) was always clear about what statistic he was presenting. Other assessments provided UCLs because they felt that these estimates were more protective of public health and safety.

Schneiderman mentioned that there were tumors in organs other than the kidney, and that, with certain additional assumptions, their risks could be added in the single-hit model, but that the required computation would be more complex in the probit model.

While much detailed information and computation was included in the risk assessments, the discussions of their authors and the CPSC Commissioners indicated that what the risk managers wanted from the assessments, and finally got, was the establishment of three facts:

- that Tris was a carcinogen,
- that Tris was absorbed by mouthing and through the skin, and that there might be significant exposure from sleepwear; and
- that there was a non-survival risk of cancer to children wearing Tris-treated garments.

This was considered sufficient to ban the use of Tris in children's garments and in treated fabric, yarn, and fiber. Even the lowest quantitative estimate of risk (7 per million) was high enough that the exact size of the risk was not critical to the regulatory decision.

Note: Work reported here is a condensed version of a chapter in: McGinnis, Bailar, Needleman, Burney. Methodologic Challenges in Risk Assessment (Working Title.) To be published, Auburn House, 1988.

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INVESTIGATION ON THE TOXICITY OF SMOKE FROM BUILDING MATERIALS AND THE CAUSES OF DEATH IN FIRE VICTIMS

Y. Alarie and F.M. Esposito
Graduate School of Public Health, University of Pittsburgh,
Pittsburgh, PA 15261

Introduction

Smoke toxicity testing was used in this study in an attempt to gain a better understanding of the cause of death in fire fatalities and gain some insight into the hazard of cyanide vs. carbon monoxide particularly for nitrogen containing polymers. Although smoke toxicity testing methods differ in their apparatus configurations and testing protocols, the fundamentals of the methods are similar, i.e. subjecting test materials to thermal stress with subsequent investigation of the toxicity of the released combustion products. The system used in the present study is a small scale model used by Alarie and Anderson (1).

Analytical assays were performed to identify and quantitate combustion products. This information was used to predict the primary toxicant released by the material under thermal stress. The physiological responses of animals were also measured during exposure to combustion products. In this study, respiration was monitored which permitted recognition of irritation, asphyxiation, convulsions and death. In addition, blood was analyzed for CO and cyanide to determine the absorbed amounts, which in turn were related to observed physiological effects. Blood concentrations of the toxicants will assist in determining the degree of poisoning attributed to a particular combustion product or help to identify the interaction of toxicants. Here we also wanted to establish the relationship of the concentration of toxicants in air and in blood.

Toxic potency of the thermal decomposition products was assessed by determining the amount of material needed to kill 50% of the animals (LC_{50}) within a 30 minute exposure and 10 minute recovery period. This parameter together with the time required for 50% lethality (LT_{50}) at the LC_{50} concentration, have been combined into a classification system which allows comparison of specimens to a reference material, Douglas fir wood (2).

Results and Discussion

Nylon 6 and a Nylon Carpet Remnant

From a series of thermal decomposition experiments on Nylon 6 (pellet form) the LC_{50} was calculated to be 6.04 g (95% C.I. of 5.76-6.33 g) and the LT_{50} was found to be 7.3 minutes.

A flame developed during the thermal decomposition of Nylon 6. The sample decomposed very rapidly during this flaming period (Figure 1). The autoignition also triggered a rapid simultaneous release of CO, HCN and CO_2 together with the consumption of O_2. Maximum concentrations of HCN, CO and CO_2 peaked at about 490 ^{o}C being 328 ppm, 4430 ppm, and 4.7% respectively during testing of an LC_{50} sample mass of 6.04 g. At the same temperature, O_2 decreased to 12.8%. Fifty percent of the animals died shortly after these events.

A house fire involving a fatality was confined to a carpeted staircase and part of the exterior wall to which it was adjoined. The fire victim was found at the foot of the staircase in the vicinity of the fire origin. A

remnant of green carpet that covered the site of fire origin and the staircase was removed and was identified microscopically and chemically to consist of Nylon fibers with a jute backing. From a series of thermal decomposition experiments on this carpet sample the LC_{50} was calculated to be 15.7 g (95% C.I. of 14.5-17-0 g). The LT_{50} was 14.2 minutes. The thermal decomposition characteristics of this carpet sample were very similar to those found for Nylon 6 as shown in Figure 1. The temperatures and duration of flaming combustion were nearly identical. The sample decomposed rapidly during flaming, but unlike Nylon 6 pellets, a non-combustible fraction remained as a residue. Correcting for the 42% residue would lower the LC_{50} mass from 15.7 to 9.1 g, close to that of Nylon 6. Peak concentrations of HCN, CO and CO_2 through decomposition of the LC_{50} mass (15.7 g) were 520 ppm, 6230 ppm and 5.7% respectively, all somewhat higher than what was found for Nylon 6. Also, O_2 decreased to 13.5%

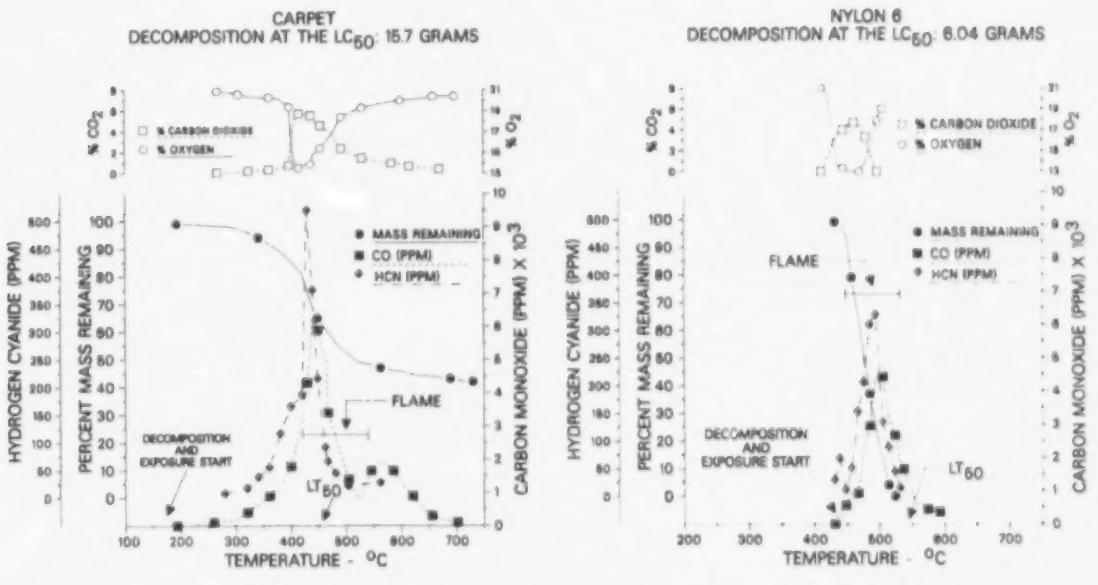

Figure 1: Data obtained during the thermal decomposition of a nylon carpet remnant and Nylon 6 when heated at a rate of 20 °C/minute

Blood samples analyzed for cyanide and COHb during two tests at the LC_{50} mass of Nylon 6 revealed mean lethal levels of 0.63 ± 0.14 mg/L cyanide and 6 ± 2% COHb. The mean blood cyanide value here was lower than that found following pure cyanide gas exposures (0.95 ± 0.17 mg/L) at the LC_{50} for this gas (177 ppm) but the value is very close to the mean of 0.59 ± 0.19 mg/L cyanide obtained during the composite LC_{50} determination of HCN combined with low O_2 environments. The COHb levels were found to be low despite ambient CO amount of >4000 ppm. These blood results in conjunction with the air analytical data seem to indicate that death can be attributed to HCN in the presence of a low oxygen environment.

The decomposition behavior of Nylon 6 at the LC_{50} mass illustrates how air and blood analytical data can be used in elucidating the toxicants responsible for death. The blood cyanide values alone would be considered

sublethal without knowing that O_2 was reduced to low levels. CO in the smoke was high, yet COHb concentrations show that very little CO was absorbed. It appears that HCN was absorbed very quickly and that the interaction of HCN and low O_2 caused a rapid toxic effect, probably on the respiratory center, that resulted in death. Because the toxic response was so fast, CO became irrelevant as evidenced by low COHb levels, despite elevated amounts in the air.

Blood samples analyzed for cyanide and COHb content throughout the LC_{50} determinations of the nylon carpet remnant revealed lethal blood cyanide levels ranging from 0.62 to 1.53 mg/L, with a mean of 1.16 ± 0.32 mg/L. The blood figures resemble those obtained during pure HCN LC_{50} gas studies in which we found a mean of 0.95 ± 0.17 mg/L (range 0.75 to 1.16 mg/L). The low blood value of 0.62 mg/L could be accounted for by the interaction of HCN-low oxygen since the O_2 level fell to 13.4% during that particular test. Lethal COHb concentrations ranged from 11 to 30% saturation, with a mean value of 26 ± 8% saturation. These values are higher than those found with pure Nylon 6, which may be related to the larger amounts of CO generated during combustion of the carpet. The jute backing probably contributed to these higher CO air levels. However, the COHb values were much lower than those found during the LC_{50} determination of pure CO gas in which the mean lethal COHb concentration was 65 ± 7% saturation with a range of 56 to 79%. Thus the relatively low COHb values and the elevated blood cyanide concentrations suggest that the cause of death of these animals is due to HCN poisoning.

Toxicological analyses of postmortem blood specimen of the victim where the fire occurred with the carpet remnant revealed a blood cyanide level of 1.2 mg/L and a COHb level less than 5% saturation. The blood cyanide concentration of mice exposed to smoke from the carpet remnant showed excellent agreement in that the mean lethal value was calculated to be 1.16 ± 0.32 mg/L for the LC_{50} determination experiments (i.e. mean value for all dead animals in experiments producing 25 to 100% lethality). However, the mice showed a higher but sublethal mean COHb level of 26 ± 8% saturation. Either the mice loaded CO faster than the human fatality (which is a well known difference) or she died before most of the CO was released.

The elevated blood cyanide in the fire victim, the lethal blood cyanide concentrations of nearly identical values in the mice, and the high concentrations of HCN released from the carpet strongly suggests that the cause of death for this fire fatality was HCN poisoning. However, the victim was charred and the primary cause of death was listed as "burns, 100% of body surface, with extensive carbonization." The pathologist who signed the death certificate was not certain if the burns occurred before or after death. Due to the low COHb level, CO had no impact on death. Since the literature is devoid of definitive lethal blood cyanide level in fire fatalities, HCN poisoning could not be listed as the principal cause of death.

All of the evidence suggests that the material responsible for this person's death was the carpet. Not only can it release sufficient quantities of HCN to produce either incapacitation or death, it also produced a large flame that would be responsible for the burn injuries, and caused depletion of O_2 and generation of CO and CO_2 as demonstrated with this small scale model.

Data simulation of a Nylon 6 Combustion Test

During further tests conducted on the LC_{50} mass of Nylon, one resulted in blood cyanide values were very much lower than those values found in other tests. The mean lethal blood cyanide was only 0.13±0.03 mg/L. In addition all four animals died rather than 50%. The mean lethal COHb level was 8±4% saturation, similar to values obtained in other Nylon 6 tests. These blood levels did not reflect intoxication by either HCN or CO alone. It was hypothesized that perhaps these gases interacted with one another or with the low O_2 atmosphere to produce the deadly environment. Thus, a series of experiments were conducted in which groups of mice were exposed to pure gases in various combinations. The purpose was to find the most toxic combination of gases, and to see if the blood cyanide and COHb concentrations measured throughout these studies would match the values found for the Nylon 6 as noted above. The air concentrations employed were those obtained during the specific combustion test in question; they were HCN, 181 ppm; CO, 6060 ppm; CO_2, 5.5%, O_2, 12.2%. The major difference between this test and the others was a lower HCN release, i.e. 181 vs 328 ppm and a higher CO release, i.e. 6060 vs 4430 ppm.

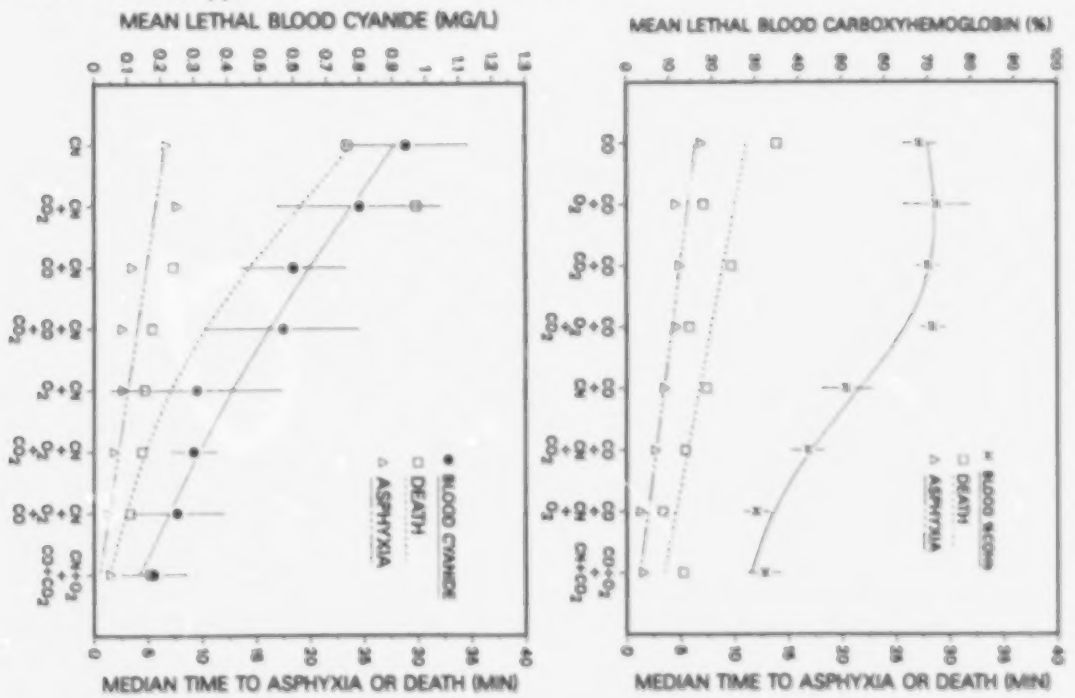

Figure 2: Mean lethal blood cyanide and carboxyhemoglobin median times to asphyxia and death at various combinations of HCN (181 ppm), CO (6060 ppm), CO_2 (5.5%), O_2(12.2%). Except for CN and CN + CO_2 where 50% lethality was observed all other combinations produced 100% lethality.

The mean lethal blood cyanide and COHb concentrations along with the median times to asphyxia and death at various test gas combinations are displayed in Figure 2. Neither the blood cyanide nor COHb level changed significantly ($p.>0.05$) when CO_2 was added to the single gases. Both CO and

HCN blood levels differed significantly ($p<.0.05$) from single gas blood contents when these gases were combined. The addition of CO_2 to a HCN-CO mixture again did not change these blood values. The lowest blood cyanide concentrations were found in the presence of HCN and low oxygen environments, with or without the company of CO and/or CO_2. In contrast, COHb levels were not affected by the presence of low oxygen, but were significantly lower when HCN was present in the gas mixtures. Finally, all four experimental gases were combined at concentrations simulating the Nylon 6 air data. The mean blood concentration of cyanide was 0.18 ± 0.10 mg/L, very close to the value of 0.13 ± 0.03 mg/L found for the Nylon 6 exposed animals. The mean COHb levels were, however, different with values of $32\pm4\%$ and $8\pm4\%$ attained for the pure gas and Nylon 6 exposures, respectively. Obviously, the mice did not absorb as much CO during combustion of Nylon 6. Nonetheless, the similarity in blood cyanide data of pure gas and Nylon 6 combustion suggests that the simultaneous release of HCN and oxygen depletion produces an environment that is rapidly lethal, even without the absorption of significant amounts of HCN.

Human Fire Fatalities

Another approach in attempting to relate small scale data to fire hazard is to compare the data to fire fatalities. Toxicological evidence gathered from actual fire victims have been available. Two such thorough studies have appeared in the literature. One study was conducted on 530 fire fatalities over six-year period in the State of Maryland (3). Another study in the United Kingdom examined 182 fatalities in a three year period (4). In the present study, postmortem toxicological concentrations of blood cyanide and COHb were examined in 136 fire deaths referred to Allegheny County, PA, USA, and 129 cases submitted to the Foundation for Fire Safety by 14 cities in the United States and Canada as shown in Figure 3. This study is not yet complete. Victims that were removed from a fire and subsequently died in a hospital were not included.

Inhalation of toxic combustion products given off during fires was responsible for about 80% of fire casualties (5). Designating 50% COHb saturation as fatal, 52, 60, and 65% of the fire fatalities would have lethal COHb levels in the United Kingdom, Maryland and the present study, respectively. Although CO appears to be the primary toxicant in a fire, these fire statistics suggest that other co-factors or gases are also responsible for many fire fatalities. These factors may include oxygen depletion, heat or burns, disease, or other fire gases. The degree of oxygen depletion during a fire is unobtainable due to a lack of biological determinants. It is difficult to assign burn injuries as a cause of death due to continued carbonization of the body after death.

An element that may be contributing to fire deaths particularly in victims with sublethal COHb concentrations is other toxic combustion products. A likely agent is hydrogen cyanide, a gas generated by thermal decomposition of nitrogen-containing materials. The importance of HCN is exemplified in the high percentage of fire victims with blood cyanide values above background levels. These percentages ranged from 58 to 84% for the above mentioned studies. Despite the recognition of CO as the primary toxicant produced during fires, HCN must not be overlooked, especially since it is nearly 20 times more toxic than CO. The number of fire casualties possessing cyanide is high, but the significance or role of HCN in fires is still unclear.

In an attempt to better understand the role of HCN in fire deaths, this study has employed controlled pure gas inhalation and combustion toxicity testing of nitrogen containing polymers on mice. The objective was to clarify several important yet unclear issues, vis-a-vis the fatal threshold value for cyanide concentrations in the blood of fire victims, the possibility of succumbing to the effects of HCN alone, and the significance of the interaction of fire gases.

We propose that a value of 1 mg/L of blood be accepted as the fatal threshold value for HCN poisoning via inhalation. The mean blood cyanide value of animals dying as a result of exposure to HCN gas was nearly 1 mg/L. A value of 50% saturation of COHb has been designated in fire death studies as the minimum CO poisoning level. This too is consistent with the mice blood data accumulated from pure gas and combustion experiments.

Figure 3 displays a scatter diagram, alike that of Anderson et al. (4), which shows the blood cyanide and COHb levels of human fire fatalities collected by the Foundation for Fire Safety and from Allegheny County. A vertical line has been placed at the accepted lethal value of COHb and a horizontal line at the proposed lethal blood cyanide level. The diagram is thus divided into four quadrants. Quadrant A represents fire deaths that can be attributed to CO poisoning. The cause of death of fire fatalities in Quadrant B ought to be assigned CO and HCN poisoning due to elevated blood concentrations of both toxicants. Presently, pathology reports indicate these victims to have died from CO poisoning only, ignoring the lethal contribution of HCN.

Many pathology reports denote the cause of death as undetermined in fire victims with less than 50% COHb. Results from this investigation indicate that blood cyanide levels >1 mg/L are lethal. Thus, those deaths in Quadrant C can be attributed to HCN poisoning, and the death certificate should reflect this toxicant.

Quadrant D represents those fire victims with sublethal blood contents of CO and cyanide. Findings with mice indicate that CO in combination with HCN can have an additive toxic effect that results in death, with sublethal blood concentrations of both toxicants. In addition, HCN and low oxygen will also show sublethal blood cyanide figures, but in most instances CO and low oxygen combinations will give sufficiently high concentrations of CO in the blood. Thus, a number of these deaths in Quadrant D can be attributed to HCN-CO combination exposures, particularly when the blood cyanide and COHb concentrations are greater than 0.5 mg/L and 40% saturation, respectively. Deaths due to HCN-low oxygen environments are also likely to occur as shown here in a small scale model. However, toxicological demonstration of the low oxygen component is impossible from postmortem blood samples. Since with CO or HCN respiratory arrest occurs while the heart is still pumping blood to the organs, there is no possibility of assessing whether or not a low oxygen atmosphere contributed to the death of the victim by measuring oxygen tension in arterial blood, even if such a sample was taken immediately at the scene of death. Furthermore, both CO and HCN depress minute ventilation prior to death and therefore O_2 uptake. Therefore, deaths occurring from a HCN-low oxygen fire atmosphere can only be speculated upon due to the lack of supporting toxicological evidence for low oxygen in blood. Finally, some of these deaths in this group may be the result of burn injuries when present or possibly some people are simply more sensitive to the combustion products of a fire. An interesting question is to what extent has HCl or other toxicants played a role in fire deaths when both COHb and blood cyanide are low. Small

scale tests are of value in pursuing this question as in investigating the role of cyanide as shown here.

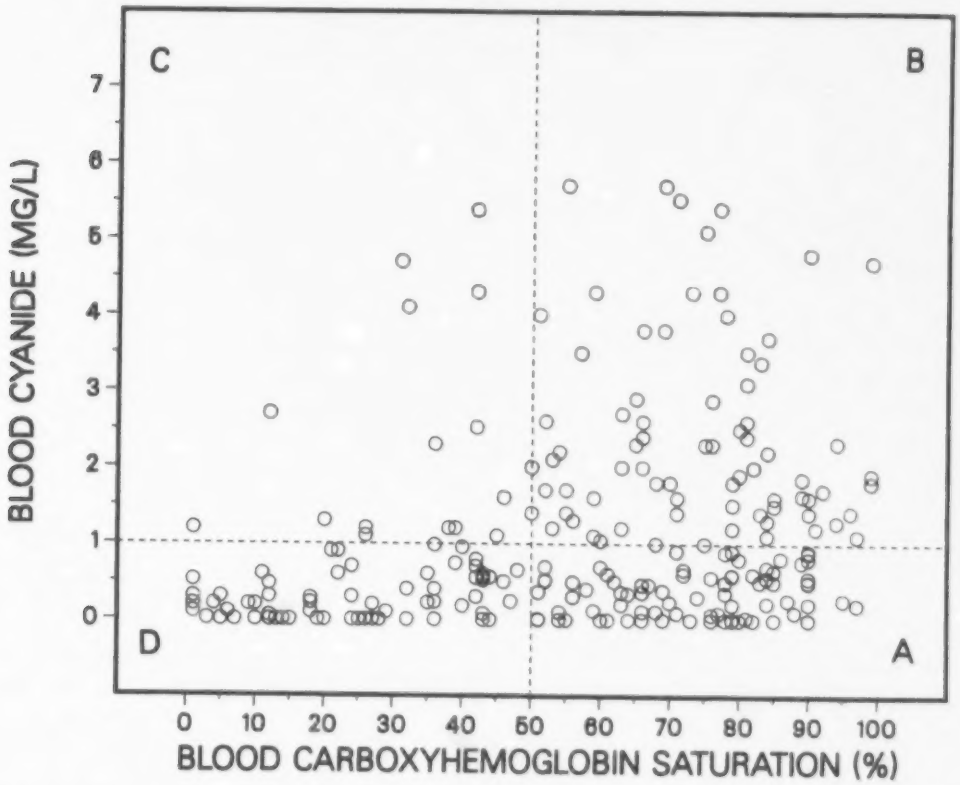

Figure 3: Lethal blood cyanide and COHb concentrations in human fire fatalities.

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LE POINT SUR LES TRIHALOMÉTHANES DANS L'EAU POTABLE

Pierre Ayotte
Ministère de l'Environnement du Québec

INTRODUCTION

C'est en 1974 que Rook (1) au Pays-Bas et Bellar et coll. (2) aux États-Unis ont découvert la présence de composés organiques volatils de la famille des trihalométhanes (THM) dans l'eau de consommation. Les THM désignent principalement quatre composés volatils: le chloroforme, le bromodichlorométhane, le dibromochlorométhane et le bromoforme. Ces études ont permis d'associer leur présence à l'utilisation du chlore dans le traitement de l'eau et ont été le point de départ d'une réévaluation de la sécurité de la chloration des eaux de consommation, une mesure de santé publique dont l'efficacité a été démontrée et qui est largement répandue dans le monde. Depuis ce temps, de nombreux travaux de recherche ont été réalisés afin d'élucider les mécanismes de formation, d'identifier d'autres sous-produits de la chloration et de déterminer les propriétés toxicologiques de ces substances.

L'intérêt porté à la présence des sous-produits de la chloration dans l'eau potable est d'autant plus grand que ces substances sont règle générale les composés organiques retrouvés en concentrations les plus élevées dans l'eau potable (3). Bien que les THM ne représentent qu'une faible proportion de tous les sous-produits de la chloration, leur surveillance est néammoins importante car leur présence indique la formation de l'ensemble des sous-produits issus de la réaction du chlore avec les acides humiques et fulviques.

Nous nous attarderons dans les lignes qui suivent à évaluer le risque pour la santé representé par la présence des THM dans l'eau de consommation. Deux composantes doivent être évaluées afin de pouvoir estimer le risque: les concentrations moyennes présentes dans l'eau potable au Québec et l'incidence des effets sur la santé (relation dose-réponse).

EXPOSITION AUX THM VIA L'EAU POTABLE

Concentrations des THM dans l'eau potable au Québec

Au Québec, le Ministère de l'Environnement, par le biais du programme des micropolluants, a accumulé de 1985 à 1987 des données concernant les concentrations de trihalométhanes présentes dans l'eau de consommation de 18 municipalités d'importance (voir la carte en annexe). Le tableau I présente les résultats obtenus lors de l'analyse des THM dans les échantillons d'eau traitée provenant de ces 18 municipalités au programme; les échantillons ont été prélevés lors de quatre campagnes d'échantillonnage (une au printemps, deux à l'été et une à l'hiver). Ces villes sont toutes munies d'une usine de filtration comportant au moins une filtration et une chloration. L'eau alimentant les usines provient du fleuve St-Laurent ou d'un de ses principaux tributaires. Les THM n'ont pas été retrouvés à l'eau brute. À l'eau traitée, le chloroforme et le bromodichlorométhane ont été détectés dans la presque totalité des échantillons. La médiane des concentrations de chloroforme (30,5 µg/l) est de loin supérieure aux concentrations médianes des autres THM. Des échantillons d'eau provenant des réseaux de distribution (à 1,5 km de l'usine) ont également été prélevés et analysés; les concentrations sont sensiblement les mêmes que celles retrouvées dans l'eau traitée à la sortie de l'usine. Comme on peut le constater au tableau II, les concentrations mesurées dans le cadre de ce programme sont similaires à celles déjà rapportées en Ontario (4) et dans d'autres études effectuées aux États-Unis (5).

TABLEAU I : CONCENTRATIONS DES TRIHALOMÉTHANES DANS L'EAU TRAITÉE PRÉLEVÉE À LA SORTIE DES USINES DE TRAITEMENT ALIMENTANT LES 18 MUNICIPALITÉS AU PROGRAMME DES MICROPOLLUANTS[a].

Trihalométhane	Pourcentage des résultats positifs (%)	Gamme des concentrations (µg/l)	Concentration médiane (µg/l)
Chloroforme	98,6	0,4-201	30,5
Bromodichloro-méthane	95,8	0,3-16,5	2,6
Dibromochloro-méthane	66,7	0,08-4,1	0,5
Bromoforme	9,7	0,11-0,2	0,2

a Concentration instantanée mesurée dans des échantillons contenant du sulfate de sodium, par la méthode "purge and trap"/chromatographie en phase gazeuse.

TABLEAU II : CONCENTRATIONS DES TRIHALOMÉTHANES TOTAUX DANS L'EAU TRAITÉE DE MUNICIPALITÉS AU QUÉBEC, EN ONTARIO ET AUX ÉTATS-UNIS

Programme	Nombre de municipalités	Nombre de résultats	Trihalométhanes (µg/l)		
			Médiane	Moyenne	Gamme
Micropolluants organiques (Québec)[a]	18	68	35	45	2 - 216
DWSP (Ontario)[b]	22	117	40	53	10 - 206
NOMS-phase 3D (États-Unis)[c]	106	--	37	53	ND - 295
AWWARF (États-Unis)[d]	727	--	39	42	ND - 360

a Programme des micropolluants organiques (Ministère de l'environnement du Québec)
b Drinking Water Surveillance Program (4)
c National Organic Monitoring Survey (5)
d American Water Works Association Research Foundation (5)

La figure 1 présente l'histogramme de fréquence des concentrations de THM mesurées dans l'eau prélevée à la sortie des usines de filtration. La plupart des résultats sont inférieurs à 100 µg/l; deux résultats approchent les 200 µg/l. En considérant l'ensemble des données, le chloroforme représente en moyenne 89% de la concentration totale des trihalométhanes, le bromodichlorométhane 10% , le dibromochlorométhane et le bromoforme moins de 2 % du total. L'exposition aux THM est donc principalement une exposition au chloroforme.

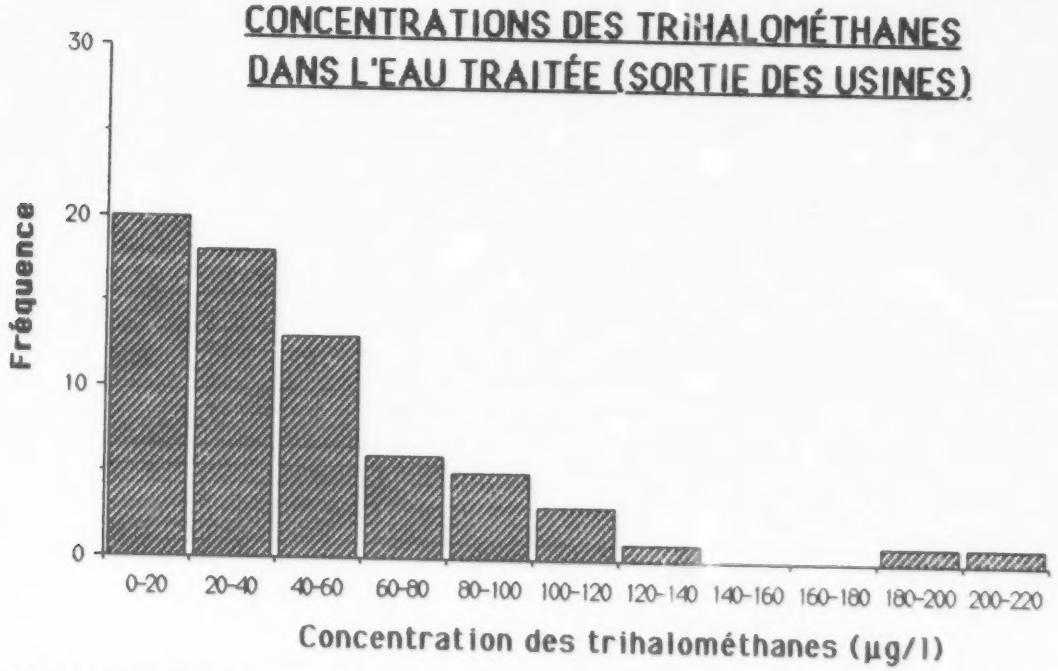

FIGURE 1: DISTRIBUTION DES CONCENTRATIONS DES TRIHALOMÉTHANES DANS L'EAU TRAITÉE PRÉLEVÉE À LA SORTIE DES USINES DE TRAITEMENT ALIMENTANT LES 18 MUNICIPALITÉS DU PROGRAMME.

Exposition globale

En considérant les données présentées ci-dessus pour les grandes municipalités, une concentration entre 30 et 40 µg/l nous semble un estimé réaliste de la concentration moyenne de THM présente dans l'eau potable au Québec. En assumant une consommation quotidienne de 1,5 l d'eau potable, l'apport quotidien de l'eau potable varierait entre 45 et 60 µg. Environ 80% de la population québécoise s'alimente en eau de surface désinfectée par l'addition de chlore, soit environ cinq millions de personnes.

Les données concernant l'exposition via l'air où la diète sont rares. En considérant les données obtenues dans d'autres pays, l'exposition totale quotidienne de la population canadienne serait en moyenne de 100 µg (6); d'autre part, l'expostion ontarienne au chloroforme a été estimée à 70 µg par jour (7). Ainsi, l'eau potable désinfectée par l'addition de chlore constitue vraisemblablement la principale source d'exposition au chloroforme ainsi qu'aux autres trihalométhanes. L'exposition globale pourrait être supérieure au niveau de 100 µg précédemment suggéré, si l'on considère l'apport possible de l'utilisation d'eau chaude (lessive, douche) aux concentrations de THM présentes dans l'air des maisons.

EFFETS SUR LA SANTÉ ET ÉVALUATION DU RISQUE

Bien que les THM et en particulier le chloroforme puissent produire toute un variété d'effets toxiques chez les animaux de laboratoire [hépatotoxicité (8, 9), néphrotoxicité (10), retard de croissance (11), immunotoxicité (12)], les doses requises pour induire ces manifestations adverses (>100 mg/kg) sont nettement supérieures à celles générées par l'expostion journalière estimée précédemment (environ 1,5 µg/kg). Pour ces réactions adverses, on assume la présence d'un niveau d'exposition "seuil" (NOEL) sous lequel aucun membre de la population exposée ne sera atteint par l'effet toxique considéré.

Cancérogénicité

L'effet sur la santé qui préoccupe le plus les intervenants en santé publique dans les cas d'expositions chroniques à de faibles quantités de THM est l'augmentation de l'incidence de cancer dans la population. Les évidences de cancérogénicité proviennent principalement d'études épidémiologiques et d'études chez les animaux de laboratoire.

Études épidémiologiques. Plus de 20 études épidémiologiques ont porté sur la relation possible entre la désinfection des eaux par le chlore et le cancer. Les données provenant d'études épidémiologiques récentes effectuées aux États-Unis, utilisant une méthodologie supérieure à celle des premières études, suggèrent une faible augmentation du risque de certains cancers (vessie, colon, rectum) associée à la consommation d'une eau désinfectée par l'addition de chlore (13). Deux études de type "case-control" où des entrevues personnelles ont été réalisées auprès des sujets à l'étude seront brièvement discutées.

La première étude est celle de Cragle et coll. (14) publiée en 1985 et qui concerne l'incidence du cancer du colon dans l'état de la Caroline du Nord. Des entrevues personnelles ont été réalisées auprès de patients hospitalisés (hommes et femmes) pour lesquels un diagnostic de cancer du colon primaire avait été posé. L'information recueillie auprès des patients concernait des facteurs de risque suspectés pour ce type de cancer, y compris la consommation d'eau chlorée, et ce pour une période couvrant 25 ans de la vie du patient. Les variables autres que la consommation d'eau potable pour lesquelles des associations positives ont été observées sont l'hérédité et la consommation d'alcool couplée à une diète riche en graisses. Le tabagisme et le nombre de grossesses montraient quant à eux des associations négatives. Une interaction a été notée entre l'âge et la consommation d'eau chlorée: au dessus de 60 ans, une relation statistiquement significative a été observée entre la consommation d'eau chlorée et l'incidence du cancer du colon, en utilisant un modèle statistique qui tient compte des autres facteurs qui pourraient avoir une influence. Dans les groupes d'âge de 60 ans et plus, le sous-groupe qui avait consommé l'eau potable chlorée de leur résidence durant plus de 16 ans montrait un rapport des probabilités supérieur à celui du sous-groupe ayant consommé de l'eau chlorée durant moins de 15 ans. Ce rapport atteint 3,36 pour les personnes agées de plus de 80 ans et qui ont consommé de l'eau chlorée durant plus de 15 ans. On ne fait aucune mention des niveaux de THM dans l'eau potable consommée par les sujets de l'étude.

La deuxième étude épidémiologique a été initiée en 1979 par le National Cancer Institute aux États-Unis et avait pour but d'examiner la relation suspectée entre le cancer de la vessie et la consommation d'édulcorants artificiels. Cantor et coll. (15) ont été en mesure d'analyser en plus l'influence de la consommation d'eau chlorée sur le cancer de la vessie. Lors d'entrevues personnelles, des informations détaillées concernant la mobilité géographique, la source d'eau potable et d'autres variables pertinentes ont été colligées. Dans un premier temps, les analyses ont été restreintes aux 1244 cas et 2500 témoins qui n'avaient jamais occupé d'emplois à risque pour le cancer de la vessie et qui avaient consommé de l'eau d'une source chlorée ou non-chlorée pendant au moins 50% de leur vie. Globalement, la comparaison entre la consommation d'une eau de surface chlorée et la consommation d'une eau souterraine non-

chlorée n'a pas révélé de différences statistiquement significatives. Toutefois, parmi les non-fumeurs qui généralement sont à faible risque pour ce type de cancer, le groupe s'alimentant en eau chlorée montrait un rapport des probabilités de 1,4 comparativement au groupe consommant de l'eau souterraine non-chlorée; de plus une relation entre la durée d'exposition et l'importance du risque a été mise en évidence. Parmi les non-fumeurs, le risque relatif passe de 1,3 pour les consommateurs d'eau chlorée durant moins de 20 ans à 2,3 pour ceux qui ont consommé de l'eau chlorée durant plus de 60 ans.

À la suite d'analyses supplémentaires des données de cette étude , Cantor et coll.(16) ont rapporté des associations positives entre le risque de cancer de la vessie et la quantité ainsi que la durée de consommation d'eau chlorée, principalement chez les sujets ayant demeuré pendant longtemps dans des communautés s'alimentant en eau de surface chlorée. L'effet de durée d'exposition était surtout évident chez les femmes, et chez les hommes non-fumeurs, principalement ceux dont la consommation d'eau potable était supérieure à la consommation médiane, le risque relatif atteignant 3,0 pour les plus de 60 ans, en comparaison avec les utilisateurs d'eau non-chlorée la vie durant.

Ces études n'ont pas éliminé la possibilité déjà soulevée (17) voulant que des paramètres de l'eau autres que les sous-produits de la chloration (pollution industrielle) soient à l'origine des résultats obtenus. Bien qu'elles supportent l'existence d'une relation causale entre l'augmentation de l'incidence de certains types de cancer et les sous-produits de la chloration, une relation de cause à effet n'a pas encore été formellement démontrée, les études épidémiologiques effectuées à ce jour étant toutes rétrospectives. Le degré de crédibilité de la relation est toutefois important, étant donné que les mêmes types de cancer (tractus gastro-intestinal et urinaire) ont été observés dans plusieurs études indépendantes, et que les résultats des études récentes suggèrent l'existence d'une relation dose-réponse (17). Finalement, les associations notées sont cohérentes avec les résultats de plusieurs études *in vitro* montrant que les concentrés d'eau potable chlorée possèdent un pouvoir mutagène qui n'est généralement pas présent dans des concentrés d'eau brute (18-20).

Les études précédemment discutées ont utilisé comme variable l'absence ou la présence de la chloration, sans tenir compte des différentes substances individuellement. Elles ne permettent donc pas de conclure quant au pouvoir cancérigène des THM comme tels chez l'homme. Certaines études écologiques ont considéré comme variable un estimé de la concentration de THM. Bien que des associations positives aient été notées dans certains cas, la nature même de ces études ne permet pas d'évaluer l'exposition individuelle des sujets. De plus, les THM ne sont pas les seuls sous-produits possiblement cancérigènes dans l'eau potable. Par conséquent, l'évaluation du risque potentiel associé à la consommation d'une eau contenant des THM doit être basée sur les données obtenues d'études examinant le pouvoir cancérigène de chaque THM individuellement,chez les animaux de laboratoire (21).

Études chez les animaux de laboratoire. Seul le chloroforme a été suffisamment étudié pour porter un jugement sur son potentiel cancérigène. Les organismes gouvernementaux tels l'Organisation mondiale de la santé et l'Environmental Protection Agency aux États-Unis ont classé cette substance parmi les composés cancérigènes pour les animaux (22, 23). Ces organismes assument l'absence d'un seuil pour l'effet cancérigène et évaluent le risque associé aux faibles concentrations en extrapolant à l'aide d'un modèle statistique conservateur à partir des données d'études chez le rat ou la souris. L'absence de seuil pour le cancer ne fait pas l'unanimité en toxicologie; cependant les organismes de santé publique ont adopté cette approche car on considère qu'elle apporte un maximum de protection pour la population.

Un autre point litigieux concerne la signification de ces résultats obtenus à la suite de l'administration de fortes doses chez les animaux de laboratoire. Des chercheurs ont en effet relevé le fait qu'aux fortes doses où un effet néoplastique (cancer du foie, des tubules rénaux) est observé, le chloroforme produit des dommages importants au niveau de ces organes cibles (24, 25). Ainsi, l'effet cancérogène d'un composé comme le chloroforme pourrait être un

phénomène secondaire à l'effet nécrotique qu'il induit. Il découle de ces observations que l'exposition à des concentrations de chloroforme qui ne produisent pas de lésions nécrotiques à l'organe cible pourrait ne pas représenter un risque cancérogène significatif pour l'homme. Ceci fait à nouveau ressortir la controverse entourant l'utilisation de fortes doses lors des tests de cancérogénicité. L'emploi de fortes doses est toutefois nécessaire si l'on veut avoir une probabilité suffisante de détecter l'effet cancérigène en utilisant un nombre raisonnable d'animaux.

Les expériences où des effets cancérigènes ont été rapportés sont résumées au tableau III. On y présente également les incidences potentielles de cancer calculées à l'aide du modèle linéaire à plusieurs étapes (21). En considérant les différentes études décrites de façon sommaire dans ce tableau, deux se prêtent davantage à l'évaluation du risque, celle du NCI (26) et celle de Jorgensen et coll. (27), car plusieurs doses ont été utilisées. Ces deux études arrivent cependant à des résultats divergents concernant la production de tumeurs hépatiques chez la souris. Bull et coll (28) ont publié des données qui suggèrent que la différence entre les résultats de l'étude du NCI et l'étude de Jorgensen et coll. concernant la présence de tumeurs hépatiques chez la souris pourrait résulter de l'emploi d'un véhicule différent. Puisque dans l'étude de Jorgensen, le chloroforme a été administré dans l'eau de boisson, ces résultats sont davantage pertinents que ceux obtenus lors de l'étude précédente. Les résultats montrant une incidence accrue de tumeurs rénales chez le rat sont donc les plus appropriés pour l'évaluation du risque. Bien que l'incidence notée soit faible, cet effet a été observé dans deux études indépendantes (26, 27) et le nombre important d'animaux utilisés conduit à un estimé du risque d'une plus grande précision (21).

TABLEAU III : RÉSUMÉ DES ÉTUDES PORTANT SUR LE POUVOIR CANCÉRIGÈNE DU CHLOROFORME ET ESTIMÉS DE RISQUE.

Animal (souche/ sexe)	Véhicule	Localisation des tumeurs	Dose (mg/kg)	Incidence	Risque estimé [a]	Référence
Rat (Osborne-Mendel/ mâle)	eau de boisson	Reins	0 19 38 81 160	4/301 4/313 4/148 3/48 7/50	2×10^{-6}	(27)
Souris ($B6C3F_1$/femelle)	huile de maïs	Foie	0 138 277	0/80 36/45 39/41	6×10^{-5}	(26)
Souris ($B6C3F_1$/mâle)	huile de maïs	Reins	0 138 277	1/77 1/50 2/45	7×10^{-7}	(26)
Souris (ICI/mâle)	Pâte dentifrice	Reins	0 17 60	0/72 0/37 8/38	6×10^{-9}	(29)

a Risque estimé à l'aide du modèle linéaire à plusieurs étapes (21); on assume une consommation quotidienne de 1 litre d'eau contenant 40 µg/l de chloroforme.

DISCUSSION ET CONCLUSION

Les questions devant être considérées dans la gestion de risques environnementaux sont (30):

- Quels sont les risques associés à l'exposition?
- Est-ce que ces risques sont acceptables?
- Comment éliminer, ou à tout le moins limiter le danger s'il est jugé innacceptable?

Il n'existe pas à l'heure actuelle de réponse claire à la première question. Le risque calculé à partir des données présentées au tableau III concernant l'incidence des tumeurs rénales chez le rat indique que le risque cancérigène du chloroforme pour la consommation la vie durant de 1 litre d'eau contenant 40 µg/l serait $2,0 \times 10^{-6}$ ($3,6 \times 10^{-6}$ pour la limite supérieure de l'intervalle de confiance à 95%).

Le risque représenté par la présence de chloroforme dans l'eau potable peut paraître faible. Cependant, le chloroforme et les autres THM ne représentent qu'une petite partie de l'ensemble des sous-produits de la chloration présents dans l'eau potable. On ignore à l'heure actuelle les propriétés toxicologiques de la majorité des autres composés organiques présents dans l'eau. La plupart des composés connus appartiennent à la catégorie des composés organiques volatils. Or, 90% des composés organiques dans l'eau potable n'appartiennent pas à cette classe; seulement 10-20% de ces composés non-volatils ont été identifiés (17). Ainsi, à l'heure actuelle, l'approche d'évaluation du risque sur la base de composés considérés individuellement ne nous apparaît pas satisfaisante pour évaluer le risque associé à des mélanges complexes dont les composantes sont encore en grande partie inconnues.

Les études épidémiologiques effectuées à ce jour sont également inadéquates pour quantifier ce risque avec précision, à cause des nombreux facteurs pouvant influer sur les résultats et du fait que l'exposition aux sous-produits de la chloration n'a généralement pas été mesurée dans ces études. Le risque relatif rapporté lorsque l'on compare grossièrement eau de surface et eau souterraine non-chlorée est faible mais considérant l'utilisation largement répandue du chlore dans le traitement des eaux de consommation, même une faible augmentation du risque relatif pour des cancers dont l'incidence est élevée (i.e. cancer du colon) pourrait avoir un impact suffisamment important sur la santé publique pour nécessiter une intervention (17).

Le choix de l'acceptabilité d'un risque relève davantage de la politique et nécessite la comparaison de ce risque à d'autres risques auxquels la population est soumise. Cependant, pour ce faire, il est nécessaire d'obtenir pour les différentes expositions un estimé relativement précis du risque réel pour la population, ce que ne permettent pas les calculs de risque présentement utilisés pour estimer à partir d'études chez les animaux de laboratoire le risque de cancer découlant d'une exposition à de faibles quantités de composés organiques (30). Certes, on peut affirmer que le risque de cancer relié à la consommation d'une eau contenant du chloroforme est nettement inférieur aux risques cancérigènes associés à la diète et aux habitudes de vie telles la consommation de cigarettes et d'alcool (30, 31). Cependant, même ces comparaisons peuvent être contestées, étant donné la perception que le population a des risques volontaires et involontaires (32).

Dans le domaine de l'eau potable, les organismes gouvernementaux ont choisi pour la plupart de considérer le risque associé à la présence d'un produit cancérigène comme à toute fin pratique négligeable s'il amène un excédent théorique de cas de cancer ne dépassant pas 1/100 000 (22, 33).

Le risque cancérogène associé à la présence du chloroforme représente un cas particulier, du fait que ces contaminants sont générés par la chloration des eaux, une mesure qui permet la désinfection des eaux et qui minimise les risques de propagation de maladies infectieuses dans la population. La désinfection des eaux est primordiale et ne doit pas être compromise pour quelque raison que ce soit. Ainsi, il ne saurait être question pour l'instant d'éliminer

l'utilisation du chlore dans le traitement de l'eau potable. Cet oxydant est un bon germicide et est assez persistant dans l'eau pour assurer le maintien d'une quantité résiduelle minimisant la possibilité de contamination bactérienne originant du réseau de distribution. Pour la post-désinfection des eaux traitées, la chloration demeure apparemment la meilleure méthode présentement disponible (34).

La réduction des sous-produits de la chloration n'est toutefois pas nécessairement incompatible avec la désinfection adéquate des eaux de consommation. L'eau destinée à la post-désinfection a déjà été débarassée en grande partie des substances précurseurs des trihalométhanes et autres sous-produits halogénés. Il ne s'agit donc pas de l'étape du traitement qui est déterminante relativement à la formation des sous-produits d'oxydation. La plus grande partie des trihalométhanes est plutôt formée lors de l'oxydation de première étape, soit lorsque le chlore est appliqué à une eau chargée de matière organique contenant les précurseurs des trihalométhanes. Une première solution consiste donc à réduire les concentrations des précurseurs en optimisant les différentes étapes du traitement à l'usine (floculation, coagulation, sédimentation, filtration) et en déplaçant le point d'injection du chlore après la sédimentation. La réduction des précurseurs a l'avantage d'abaisser la demande totale en désifectant et donc de réduire la possibilité de formation de tous les sous-produits de la désinfection (35, 36) tout en améliorant l'efficacité de la désinfection (21).

Une deuxième solution serait de ne pas utiliser le chlore en oxydation de première étape (35). D'autres substances peuvent être utilisées, telles l'ozone ou le bioxyde de chlore, mais des interrogations subsistent quant aux sous-produits générés par ces oxydants. Les chloramines peuvent également être utilisées; aux États-Unis, la chloramination est parmi les solutions les plus fréquemment employées pour abaisser les concentrations de THM (5). Parmi les oxydants considérés en remplacement du chlore lors de l'oxydation de première étape, l'ozone semble un candidat de choix. En terme de risque cancérigène, l'ozone n'a pas fait l'objet d'études approfondies comme c'est le cas pour le chlore. Cependant, cet oxydant n'engendre pas la formation de sous-produits chlorés et n'augmente généralement pas le pouvoir mutagène de l'eau tel qu'évalué par des tests *in vitro* (19, 20). De plus, ses propriétés germicides sont supérieures à celles des autres oxydants, notamment vis-à-vis les virus et les organismes pathogènes problèmatiques à l'heure actuelle (*Giardia lamblia*; 21).

Une troisième solution consiste à éliminer les sous-produits après leur formation, soit par aération ou par adsorption sur du charbon actif. L'aération ne permet que de réduire les concentrations des THM et des autres composés volatils, mais n'affecte en rien les concentrations des produits non-volatils qui forment la majorité des sous-produits de la chloration. L'utilisation de charbon actif, en plus de permettre la diminution des concentrations de nombreux micropolluants organiques, constitue également un moyen efficace pour réduire les précurseurs (36). Des trois solutions envisagées, l'utilisation d'autres oxydants semble la plus efficace et la moins coûteuse.

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ANNEXE

PROGRAMME DES MICROPOLLUANTS

CAMPAGNES D'ÉCHANTILLONNAGE 1985 À 1987

STRATÉGIE QUÉBÉCOISE CONCERNANT L'ÉTUDE DE LA QUALITÉ DE L'AIR DANS LES ÉDIFICES À BUREAU

Par

M. Jean-Claude Dionne
IRSST

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The Characterization and Identification of Pesticides and Areas Vulnerable to Groundwater Contamination by Pesticides in Canada

Blair McRae, Agriculture Canada, Pesticides Directorate
Issues, Planning and Priorities Division, Ottawa

Groundwater is a valuable natural resource and is essential to our livelihood in providing water for drinking and other purposes. Over 6.2 million Canadians (or 26% of the population) rely on groundwater for domestic purposes.

Pesticides have made great contributions to our society. However, their widespread use can lead to the contamination of our precious groundwater resource. Pesticide residues have been detected in well water across Canada; aldicarb in Quebec, Ontario, Prince Edward Island and New Brunswick, alachlor and atrazine in Ontario, and picloram has been detected in surficial sand aquifers in Saskatchewan and Quebec.

In order to assess the full scope of and develop appropriate strategies for groundwater contamination, more detailed monitoring studies are needed. In designing such studies, it is important to understand the various factors that affect the leaching potential of pesticides. The current project is designed to contribute to this understanding by combining four areas of information:

1) a rating list of potentially leachable pesticides;
2) soil and landscape attributes favouring leaching;
3) groundwater aquifer information; and
4) data on cropping practices.

The pesticides were rated on the basis of their potential to contaminate groundwater (solubility, persistence, volatility), their volume of use and their overall regulatory concerns (extent of use, age and completeness of supporting data, exposure to humans and the environment, special concerns and known contaminants).

The soil landscape information is presented in the form of maps at a scale of 1:2,000,000. The maps are based on permanent soil, non-soil (or rock) and landscape attributes. The attributes mapped were: slope gradient (1-3% and 4-9%), depth to water table (0-3 m and > 3 m), soil texture (sand and sandy loam) and surface formation (hummocky, level, knoll and kettle and undulating). These attributes and their classes help to characterize areas across the country that are vulnerable to the leaching of pesticides to groundwater. The vulnerable areas were further characterized and delineated by overlaying the locations of major surficial and bedrock aquifers on the maps.

The cropping practices information for the identified vulnerable areas and the priority pesticides registered for the crops are identified in appendices of the report. The information in these appendices is linked through a numbering system to the vulnerable areas on the maps.

A number of other environmental and agricultural factors affecting the leaching of pesticides to groundwater are characterized in the report. The site specific nature of a number of these factors prevented compiling and providing the data for them at a national level in this report.

This project will prove useful to industry, researchers and various government agencies to help identify target areas and priority pesticides for monitoring, audit and/or investigation programs.

MICROPOLLUANTS ORGANIQUES DANS L'EAU DE CONSOMMATION

Michel Larue, Pierre Ayotte et François Messier
Ministère de l'Environnement du Québec

C'est en mai 1985 que le ministère de l'Environnement du Québec débutait son programme d'analyse des micropolluants organiques dans les eaux brutes et et les eaux traitées de dix-huit (18) municipalités du Québec desservant en eau potable près de 2,5 millions de personnes. Deux campagnes sont effectuées annuellement: une à l'été et l'autre à l'hiver. Les familles de paramètres suivantes ont été analysées: les biphényles polychlorés (trois premières campagnes seulement), les hydrocarbures polycycliques aromatiques (HPA), certains composés organiques volatils, des insecticides de la famille de organo-phosphorés et des herbicides de la famille des triazines. Ce programme des micropolluants nous permet d'orienter nos efforts de surveillance et de recherche sur les paramètres qui sont les plus susceptibles de porter atteinte à la santé publique.

BIPHÉNYLES POLYCHLORÉS

Les biphényles polychlorés n'ont été retrouvés dans aucun des échantillons prélevés au cours des trois premières campagnes d'échantillonnage, le seuil de détection étant de 10 ng/l.

HYDROCARBURES POLYCYCLIQUES AROMATIQUES

Les eaux brutes montrent dans certains cas des concentrations quantifiables de HPA. Les systèmes de traitement semblent toutefois efficaces pour réduire leur concentration à des niveaux en général inférieurs au seuil de quantification (5 ng/l). Toutefois, les résultats suggèrent que les canalisations de certains réseaux de distribution introduisent des HPA dans l'eau potable. Les concentrations retrouvées varient de 1 à 288 ng/l pour la somme de six HPA représentatifs; la médiane des concentrations est de 10,6 ng/l. La valeur indicative fixée par l'Organisation mondiale de la santé en 1971 est de 200 ng/l pour la somme des concentrations de ces six HPA.

Le benzo (a) pyrène est le seul HPA pour lequel Santé et Bien-être social Canada recommande une concentration maximale acceptable (10 ng/l); ce composé n'a été détecté que deux fois dans l'eau des réseaux de distribution, à une concentration inférieure à 5 ng/l.

COMPOSÉS ORGANIQUES VOLATILS

Les composés organiques volatils qui ont été détectés dans l'eau traitée sont par ordre décroissant de fréquence: les trihalométhanes (99%), le tétrachloroéthylene (18%), le dichlorométhane (12%), le toluène (11%), le 1,1,1-trichloroéthane (9%), le trichloroéthylène (8%), le benzène (4%) et le 1,2-dichloroéthane (2%). À l'exception des trihalométhanes, les concentrations mesurées sont faibles et dans la plupart des cas inférieures à 1 ug/l. Pour les les trihalométhanes, la gamme de concentrations rencontrée varie entre 1,6 et 215,6 ug/l, la médiane étant de 35,3 ug/l. La norme du Règlement sur l'eau potable en vigueur au Québec est de 350 ug/l.

PESTICIDES

Les pesticides retrouvés dans l'eau de consommation sont l'atrazine, la simazine et la cyanazine. C'est toutefois l'atrazine, un herbicide utilisé dans la culture du maïs, que l'on détecte le plus souvent dans l'eau traitée (79% des échantillons) et dont les concentrations mesurées sont les plus élevées. La gamme de concentrations de cet herbicide pour les résultats positifs s'échelonne entre 0,03 et 1,91 ug/l, la médiane étant inférieure à 0,1 ug/l. La recommandation intérimaire de Santé et Bien-être social Canada concernant la concentration maximale admissible de cet herbicide dans l'eau potable est 60 ug/l.

CONCLUSION

Les résultats de ces campagnes d'échantillonnage montrent que plusieurs micropolluants sont présents dans les eaux de consommation au Québec. Les concentrations retrouvées sont souvent infimes et voisines du seuil de détection des méthodes analytiques. De plus, pour les HPA, la plupart des composés organiques volatils ainsi que pour les pesticides pour lesquels des données sont disponibles, on constate que l'apport de l'eau potable à l'exposition totale est faible comparativement aux autres sources comme l'air ou l'alimentation.

Les trihalométhanes représentent un cas particulier, tant par la fréquence élevée de détection que par l'importance relative des concentrations mesurées et le pourcentage élevé de l'exposition totale représenté par l'ingestion d'eau potable. Les niveaux rencontrés se rapprochent dans plusieurs cas des normes ou recommandations émises par différents organismes, d'où l'intérêt d'exercer une surveillance accrue de ces sous-produits de la chloration et d'apporter au besoin des correctifs aux méthodes de traitement de l'eau potable.

LA GESTION DES LIEUX CONTAMINÉS PAR DES SUBSTANCES DANGEREUSES AU QUÉBEC

Claudette Journault

Ministère de l'Environnement du Québec

La gestion des lieux contaminés par des substances dangereuses au Québec comporte deux aspects : les lieux d'élimination de déchets dangereux et les terrains contaminés par des substances dangereuses.

LES LIEUX D'ÉLIMINATION DE DÉCHETS DANGEREUX

Le ministère de l'Environnement a créé le programme "GERLED" qui a comme objectif environnemental, de réduire les effets négatifs que les lieux d'élimination de déchets dangereux représentent pour le milieu, de façon à protéger la santé publique et l'environnement.

L'inventaire et la caractérisation préliminaire ont constitué la première étape du plan d'intervention retenu pour gérer les lieux inventoriés. Les autres étapes de ce programme, par lequel le Ministère poursuivra son intervention au cours des prochaines années sur tous les lieux inventoriés, sont les suivantes : la caractérisation exhaustive des lieux d'élimination, l'élaboration et le choix des solutions, la réalisation de mesures correctives, le contrôle et l'évaluation des mesures correctives et le suivi environnemental.

Les principes d'action

Le Ministère oriente d'abord ses actions vers les lieux qui constituent une menace sérieuse pour la santé et l'environnement. Lors de l'inventaire, chaque lieu a été classé selon le risque potentiel qu'il représente pour la santé publique et pour l'environnement.

Des 326 lieux actuellement inventoriés, 64 font partie de la catégorie I, c'est-à-dire, les lieux présentant actuellement un potentiel de risque pour la santé publique et/ou un potentiel de risque élevé pour l'environnement, 98 lieux font partie de la catégorie II, c'est-à-dire, les lieux présentant actuellement un potentiel de risque moyen pour l'environnement et/ou un faible potentiel de risque pour la santé publique et finalement, 164 lieux sont classés catégorie III, c'est-à-dire, les lieux présentant actuellement un faible potentiel de risque pour l'environnement mais aucun risque pour la santé publique.

Les priorités d'action ont d'abord et avant tout été déterminées à partir de cette classification préliminaire. Le ministère de l'Environnement applique le principe du pollueur payeur.

Le plan d'intervention

Le plan d'intervention préconisé en est un par étape où le Ministère et le responsable de la contamination demeurent en contact tout le long du processus.

Les réalisations à ce jour

Depuis le début du programme, plus de 80 dossiers ont été traités à une ou plusieurs étapes du programme d'intervention.

Un suivi environnemental a, d'autre part, été entrepris dans l'ensemble du Québec sur les prises d'eau individuelles et collectives, potentiellement menacées par la présence d'un lieu (programme Gerled eau potable). Des analyses spécifiques sont effectuées ou le seront sur 85 lieux.

LES TERRAINS CONTAMINÉS PAR DES SUBSTANCES DANGEREUSES

Au cours des dernières décennies, un processus de fermeture et de démantèlement de complexes industriels vétustes s'est amorcé en Amérique du Nord. Le phénomène, clairement perceptible aujourd'hui, s'accélérera dans les années futures.

En cours de production, plusieurs de ces complexes industriels ont, pendant des dizaines d'années, utilisé ou généré des substances dangereuses. À la suite de rejets liés aux opérations journalières, de déversements accidentels ou de leur enfouissement pur et simple dans les cours d'usine, ces substances ont pu contaminer le sol et l'eau souterraine environnants.

À l'heure du démantèlement, il est nécessaire de se pencher sur ce type de contamination afin d'évaluer le besoin de statuer sur d'éventuelles restrictions aux usages de ces terrains et sur la pertinence d'y entreprende des travaux de restauration.

Cette démarche est d'autant plus importante qu'un grand nombre d'anciens terrains industriels sont soumis au développement par des promoteurs et sont susceptibles d'être utilisés à des fins nouvelles (construction de quatiers résidentiels, de commerces, de parcs, etc.).

Au Québec, plusieurs propriétaires et promoteurs désireux de vendre ou de réhabiliter d'anciens terrains industriels se sont récemment adressés au ministère de l'Environnement afin d'obtenir conseil sur la nécessité d'excaver des sols contaminés et de connaître les niveaux de décontamination à atteindre avant de les aménager.

Parallèlement, de multiples intervenants, industriels, consultants, groupes de pression de même que la population en général, ont manifesté leur intérêt concernant l'adoption par le Gouvernement d'une politique d'ensemble régissant le devenir de ces terrains contaminés.

Dans un premier temps, des critères d'évaluation de la contamination des sols et de l'eau souterraine ont été établis, à la suite d'une consultation menée auprès des autorités compétentes de divers pays industrialisés déjà aux prises avec un problème similaire. L'utilisation de ces critères, jumelée à la connaissance des propriétés hydrogéologiques des sols concernés, de l'aire de dispersion et des propriétés éco-toxicologiques des contaminants ainsi que du type de réemploi projeté, a déjà permis de déterminer pour certains projets en cours, le niveau de décontamination à atteindre afin d'assurer un développement sécuritaire.

La détermination des niveaux de décontamination à atteindre ne constitue que l'un des moyens permettant de résoudre les problèmes causés par la présence des sols contaminés.

Le ministère de l'Environnement oeuvre activement dans ce dossier et plusieurs outils sont actuellement développés pour faire face à ce problème.

CONCLUSION

La gestion des lieux contaminés par des substances dangereuses constitue un nouveau domaine voué à un développement rapide. Au cours des prochaines années, nous assisterons sans doute à la naissance d'une industrie nouvelle, celle de l'assainissement des sols.

De nombreux défis technologiques et financiers sont à relever dans ce domaine. Le monde scientifique est appelé à parrainer cette industrie de pointe.

SURVEY AND EVALUATION OF URANIUM IN PORT HOPE SEWAGE SLUDGE AND IN SOILS FERTILIZED WITH PORT HOPE SLUDGE

D.L. Lush and P.M. McKee
Beak Consultants Limited, Mississauga, Ontario

Until 1985, sludges from the Port Hope Water Pollution Control Plant (WPCP) were used as agricultural fertilizers, under guideline limits set by the Ontario Ministries of Agriculture and Food, Environment, and Health. A subsequent sampling program showed these sludges to contain uranium, and identified the principal source as a uranium refinery. In the absence of guidelines for land application of sludges containing U, landspreading activities were suspended and sludge has been stockpiled. A study was undertaken to compare concentrations of U and its decay products in Port Hope sewage sludges with concentrations in sludges from other regional WPCPs, evaluate U accumulation in sludge-amended soils, measure accumulation in food crops and other plants, and use these measurements to quantify the implications to human health and agricultural crops.

U concentrations in the Port Hope sludges averaged 6 ppm, and were higher than the 0.25 ppm or less in other WPCP sludges. Levels of U-238 decay products were slightly elevated in the Port Hope sludges relative to other sludges. In soils from farms having a history of very high application rates of Port Hope sewage sludge, U concentrations ranged between 1.9 and 12.9 ppm, although only one sample showed concentrations above 3.1 ppm. Concentrations in control soils were 1.0 to 2.3 ppm.

U and U-238 decay products occurred at much lower concentrations in Port Hope sewage sludge than in typical inorganic phosphate fertilizers. However, radionuclide application rates would be higher in soils fertilized with Port Hope sewage sludge, due to the large volumes required for effective fertilization. If this sludge was applied at the rate recommended by the provincial sludge utilization guidelines, based on inorganic nitrogen content, concentrations added to surface soil every five years would be 0.85 ppm for U and 0.1 to 0.4 $mBq \cdot g^{-1}$ for U-238 decay products. These are less than typical background concentrations of about 2 ppm for natural U and 25 $mBq \cdot g^{-1}$ for members of the U-238 decay series. The implication of long-term use of Port Hope sludge on soils are evaluated in conjunction with accumulation rates of other trace metals.

Edible plant tissues, sampled from sludge-treated fields and stockpiled Port Hope sludges, generally had U concentrations below the 0.2 ppm dry weight detection limit, including tomatoes growing on undiluted sludge. Leaves and stems had slightly higher U concentrations, while roots typically showed the highest concentrations (up to 4 ppm dry weight). The geometric mean soil-to-plant transfer coefficient for U was 0.0063 for all tissues (fresh weight plant-dry weight soil basis).

The effective dose equivalent attributed to sludge use received by a hypothetical farmer fertilizing his fields with Port Hope sewage sludge at the rate prescribed by the provincial guidelines, and consuming crops from these same fields, is estimated at 0.00059 $mSv \cdot yr^{-1}$ for soils treated over one five-year period. A dose of 0.0056 $mSv \cdot yr^{-1}$ would be received by a farmer whose fields have been fertilized until soil uranium concentrations reach 10 ppm, achieved only after 50 years or more of sludge application. These doses are small fractions of the natural background radiation dose of about 2 mSv received annually by members of the general public, and are considered

trivial based on national and international criteria. The intake of U from ingestion of crops grown on these fields would be low relative to quantities identified as safe from a chemical toxicity perspective. Therefore, use of the Port Hope sewage sludge at rates prescribed by the sludge utilization guidelines does not result in a significant health risk to individuals exposed to the sludge from either a radiological or chemical toxicity perspective.

The maximum concentration of U in soil that should not elicit chemical toxic effects in crops is thought to be 10 ppm. This concentration would only be reached after 50 years or more of sludge application, assuming no weathering losses from soils. The time required to reach the maximum acceptable concentrations of other metals in soils from the use of sludge at concentration limits set in the provincial guidelines is similar to the time required to reach soil U concentrations of 10 ppm. Accordingly, U in Port Hope sewage sludge poses no greater concern in terms of plant toxicity than do other metals found in sewage sludges at the concentration limits designated as acceptable for land application.

Note: This project was sponsored by the Atomic Energy Control Board.

SENSIBILITÉ DES ALEVINS VÉSICULÉS DU SAUMON ATLANTIQUE À L'ACIDITÉ ET À L'ALUMINIUM

Couture, P., Parent, L., Campbell, P.G.C. et Dubreuil, B.

INRS-Eau, C.P. 7500, Sainte-Foy, Québec G1V 4C7

L'effet du pH sur la toxicité et la bioaccumulation de l'Al a été étudié en conditions contrôlées chez des alevins vésiculés du saumon de l'Atlantique (Salmo salar). Nous avons développé une approche permettant de vérifier l'hypothèse d'une augmentation de la biodisponibilité de l'Al.

Les expériences furent réalisées en:

i) travaillant sous des conditions de température, de pH et de [Al] voisines de celles rencontrées lors du choc acide au printemps;
ii) utilisant des alevins vésiculés de façon à éviter des apports de nourriture et en incubant les alevins dans une eau synthétique de façon à calculer la répartition des diverses formes d'Al monomère organique;
iii) utilisant un dispositif d'incubation sans gravier afin de permettre un suivi constant de la mortalité chez les alevins;
iv) procédant à des mesures d'adsorption et d'accumulation de l'Al intracellulaire afin d'évaluer les quantités d'Al adsorbé et absorbé;
v) mesurant les concentrations d'Al dans les alevins durant une période de dépuration afin de vérifier s'il existe des mécanismes permettant de réduire les quantités d'Al pris en charge.

Deux souches d'alevins furent utilisées. L'une provenait de la rivière Trinité alors que l'autre provenait de la rivière aux Rochers. Le dispositif expérimental comprenait trois auges où 50% du volume d'eau était renouvelé à chaque jour. La température était maintenue à 1°C et des pompes assuraient une recirculation constante de l'eau. Les autres conditions dans les auges étaient les suivantes:

auge 1: pH = 6.7;
auge 2: pH = 5;
auge 3: pH = 5; [Al] = 100 $\mu g.L^{-1}$ (concentration nominale).

Les paramètres suivants étaient mesurés à chaque jours:

- pH;
- fluorure;
- carbone organique dissous;
- conductivité;
- aluminium total (Al_T: échantillon acidifié et non filtré);
- aluminium dissous (Al_D: échantillon filtré sur membrane de 0.4 µm et acidifié);
- aluminium monomère organique dissous (Al_{CV+R}: aluminium réactif au catéchol violet après passage sur une résine échangeuse de cations).

La mortalité et la cinétique d'accumulation de l'Al ont été suivies durant une période de 17 jours alors que la dépuration le fut au cours des 18 jours qui suivirent. Juste avant le début de la dépuration, des alevins furent mis en

contact avec un agent complexant (EDTA 10^{-5}M) afin de discriminer entre l'Al adsorbé (extractible à l'EDTA) et l'Al absorbé (non extractible à l'EDTA).

Une contamination en Al a été mise en évidence dans les auges de contrôle (1 et 2). La répartition des diverses formes d'Al monomère inorganique dissous ($Al_{CV} - Al_{CV+R}$) aux diverses conditions d'exposition fut calculée à l'aide d'un modèle d'équilibre chimique (MINEQL). Dans l'auge 1, à pH 6.7, l'Al se trouve à 96% sous la forme $Al(OH)_4^-$ et seulement 4% sous la forme $Al(OH)_3^0$. Cependant, dans les auges 2 et 3, les calculs indiquent la présence de plusieurs autres formes monomères dont la forme ion libre (Al^{3+}) qui est priviligiée (29%). Étant donné que les concentrations en fluorure étaient inférieures à la limite de détection de la méthode, nous avons fixé ces concentrations à 2.7×10^{-7}M (i.e. limite de détection x 0.5) pour les besoins du modèle. À cette concentration, 21% de l'Al est sous forme de fluoro-complexes (AlF_2^+).

Dans les auges 2 et 3, les concentrations en Al monomère inorganique sont suffisamment élevées (auge 2: 15-21 $\mu g.L^{-1}$; auge 3: 41-65 $\mu g.L^{-1}$) pour provoquer un stress chez les poissons. Pour ce qui est des concentrations en Al, la valeur moyenne de 133 $\mu g.L^{-1}$ dans l'auge 3 se situe au-dessus des valeurs indicatrices de 80-100 $\mu g.L^{-1}$ d'Al total, qui, selon Van Coillie et al. (1983), provoquent une toxicité sous-létale chez les tacons de salmonidés en eaux oligotrophes.

Nos résultats montrent une mortalité accrue (6%) dans l'auge 3 par rapport à la mortalité (1%) dans l'auge 2. La mortalité pourrait être attribuable aux taux élevés de prise en charge de l'Al par les alevins: 60% de cet Al serait extractible à l'EDTA, soit présumément adsorbé aux membranes exposées. Les teneurs en Al dans les alevins de la rivière aux Rochers sont plus élevées que celles dans les alevins de la rivière Trinité. Les teneurs plus élevées dans les alevins de petite taille (rivière aux Rochers) peuvent être attribuées au fait que chez cette souche le rapport surface/volume est plus grand que chez la souche de la rivière Trinité.

Les facteurs de concentrations calculés en terme de rapport (i.e. concentration moyenne de prise en charge par les alevins ($\mu g.g^{-1}$) / concentration en Al monomère inorganique ($\mu g.mL^{-1}$) sont plus faibles à pH 5 qu'à pH 6.7. Ces résultats suggèrent qu'en condition acide, il existe une compétition entre les formes cationiques d'Al et l'ion H^+ pour accaparer les sites de complexation sur les surfaces exposées. En ce qui concerne la relation entre les formes d'Al et leur bioaccumulation, nous ne sommes pas en mesure de préciser laquelle des formes serait préférentiellement responsable de la bioaccumulation.

Durant la période de dépuration, la spéciation de l'Al est semblable dans les auges 2 et 3. L'Al lié aux poissons durant la période d'exposition contribue à la concentration plus forte en Al dans l'auge 3 par rapport à l'auge 2. On détecte une désorption significative de l'Al des alevins quelques jours après le début de la dépuration. Des recherches complémentaires devraient être effectuées pour préciser les mécanismes chimiques et/ou physiologiques de la désorption de l'Al. L'existence de tels processus pourrait amoindrir les effets des concentrations élevées en Al lorsqu'elles sont ponctuelles.

BIOTESTS CONVENTIONNELS ET EVALUATION DES DANGERS : OPTIMISATION DE L'OUTIL BIOANALYTIQUE

I.GUAY[1], C.THELLEN[2], P.COUTURE[1]

[1] INRS-EAU, Ste-Foy, Québec
[2] MENVIQ, Ste-Foy, Québec

Il est maintenant généralement accepté que les règlementations sur les effluents doivent tenir compte non seulement de la composition chimique mais aussi des réponses biologiques obtenues des biotests, la toxicité. Plusieurs types de bioessais sont normalisés et utilisés couramment mais il reste qu'ils donnent une valeur de toxicité relative, souvent unique et généralement ponctuelle qui ne considère pas le devenir de cette toxicité une fois dans le milieu. De cette façon, certains facteurs importants ne sont pas pris en compte lors du dosage de la toxicité en laboratoire : (1) l'influence du milieu récepteur; interactions entre les divers constituants de l'effluent et de l'eau réceptrice, capacité assimilatrice du plan d'eau, (2) les propriétés du contaminant; dégradabilité potentielle, persistance, accumulation, et (3) la réponse de compensation possible des organismes face à une agression toxique; récupération et acclimatation.

A cet effet, nous avons cherché à construire un schéma de procédures de dépistage qui, associé aux biotests conventionnels et complété par des analyses chimiques, permet d'obtenir une interprétation environnementale plus fiable. Dans ce contexte, il apparait important de discuter et de définir la limite d'application ainsi que la portée environnementale de ces procédures. Ces objectifs sont atteints principalement en déterminant la toxicité (algues et Microtox) d'un effluent de pâtes et papiers et dans certains cas d'un effluent synthétique persistant.

Nos résultats montrent qu'une approche intégrée d'évaluation de la toxicité est essentielle pour une gestion améliorée.

LE LAC SAINT-FRANÇOIS: BAROMÈTRE DE LA POLLUTION TRANSFRONTALIÈRE PROVENANT DU LAC ONTARIO ET DU SECTEUR INTERNATIONAL DANS LE TRONÇON QUÉBÉCOIS DU FLEUVE SAINT-LAURENT

H. Sloterdijk

Environnement Canada, Direction des eaux intérieures, 1001 Pierre Dupuy, Longueuil, Qc, J4K 1A1.

RÉSUMÉ

Un des problèmes majeurs concernant le fleuve Saint-Laurent est la dissémination des substances toxiques qu'il contient (1). La partie québécoise du fleuve est de ce point de vue affectée par deux sources principales:
- Le lac Ontario et le tronçon international Kingston-Cornwall;
- Le Corridor Montréal-Sorel.

La première, le sujet de cette présentation, contribue à l'existence d'une pollution transfrontalière transportée sur de longues distances, et le lac Saint-François est à cet égard une région clé. Le fleuve pénètre au Québec par l'élargissement que constitue ce lac; à l'exception de Cornwall, aucune industrie n'y est présente sur ses rives ou sur celles de ses tributaires. La région industrielle de Valleyfield est située trop en aval pour contribuer de manière importante à la contamination de ce plan d'eau.

Les contaminants qui pénètrent dans le lac Saint-François peuvent s'y déposer ou continuer leur migration vers l'aval; l'étude de leur devenir nous renseigne sur ce transport à distance des polluants provenant du bassin des Grands Lacs.

Les études menées depuis quelques années sur la distribution des substances toxiques (Hg, BPC, mirex, HPA et autres) dans les différents compartiments (sédiments, poissons, eau) du fleuve ont permis d'en évaluer de façon qualitative à la fois le transport et le devenir (2, 3, 4).

Nos conclusions peuvent se résumer ainsi:

1. Le lac Ontario est une source importante de polluants organiques persistants tels que les composés organochlorés (BPC, mirex, HCB, DDT, dieldrine, dioxine), ce qui n'est pas le cas pour les métaux lourds ou d'autres polluants inorganiques; ceci est confirmé par les teneurs élevées en BPC et la présence de mirex, HCB et DDE que l'on rencontre dans tout le lac.

2. Certaines sources locales sont plus importantes que le transport à longues distances provenant du lac Ontario. Ainsi les teneurs élevées en mercure identifiées le long de la rive nord sont entièrement dues aux activités industrielles dans la région de Cornwall. En outre, les teneurs très élevées de BPC et de HPA le long de la rive sud et dans l'extrémité est du lac sont dues à des sources industrielles se trouvant dans la section internationale du fleuve, notamment dans la région de Massena (N.Y.).

3. Le lac ne constitue pas un réservoir d'accumulation permanente; une fraction importante des contaminants finit par progresser vers Montréal. La morphologie, le système de courant et les vents dominants font que ce lac est sous l'influence de conditions dynamiques plus fluviales que lacustres. La prédominance de la fraction sableuse confirme cette caractéristique.

4. Nous n'avons pas trouvé d'évidence de la présence à des niveaux significatifs, d'autres contaminants caractéristiques des Grands Lacs, tels que les chlorophénols et les chlorobenzènes; toutefois des études complémentaires, portant notamment sur les dioxines, les furanes et le toxaphène, devraient nous renseigner sur ce point.

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L'UTILISATION DES PETITS POISSONS COMME BIOINDICATEURS DES SUBSTANCES TOXIQUES DANS LE MILIEU AQUATIQUE

J. Bureau et H. Sloterdijk

Environnement Canada, Direction des eaux intérieures, 1001 Pierre Dupuy, Longueuil, Qc, J4K 1A1.

Un des principaux mandats de la Direction des eaux intérieures et des terres (DEI-T) d'Environnement Canada au Québec est la surveillance de la qualité de l'eau du fleuve Saint-Laurent. Cette surveillance vise le contrôle des substances toxiques, dont la présence est une des causes majeures de la dégradation de la qualité du fleuve. Cependant, l'approche traditionnelle qui consiste à mesurer les concentrations des toxiques dans l'eau, s'est avérée insatisfaisante. Bien que l'utilisation des sédiments nous renseignent sur le transport et le devenir des substances toxiques, les poissons sont des indicateurs par excellence pour l'évaluation des tendances spatio-temporelles des contaminants lipophiles et persistants.

Jusqu'à maintenant, on a surtout utilisé les poissons adultes comme bioindicateurs de pollution organique et inorganique. Toutefois, les effets d'âge, de variations du régime alimentaire et du cycle reproductif et de dispersion géographique ont entrainé une très grande variabilité dans les résultats analytiques. Pour ces raisons, il était très difficile de les utiliser pour une évaluation rigoureuse des tendances aussi bien spatiales que temporelles dans les plans d'eau étudiés.

Dans le but de mieux cerner ces tendances, La Direction des eaux intérieures décida de compléter son programme de surveillance des substances toxiques en initiant une série d'études menées en 1979 (1), 1984 (2), 1986 (3) et 1987, inspirées des travaux déjà effectués en Ontario, et basées sur l'utilisation des petits poissons de l'année comme bioindicateurs. Compte tenu de son ubiquité dans la zone d'étude (tronçon Cornwall-Portneuf du fleuve Saint-Laurent), on opta pour le queue à tache noire (Notropis hudsonius; spottail shiner) comme espèce cible.

Les poissons, récoltés à l'aide d'une seine à maille fine, ont d'abord été identifiés, puis regroupés en échantillons de plusieurs dizaines d'individus chacun qui furent acheminés au laboratoire pour homogénéisation et analyse. Dans le cas où le queue à tache noire s'avérait absent de certains biotopes, on évalua la possibilité d'utiliser la perchaude (Perca flavescens; yellow perch) comme espèce de remplacement. Lorsqu'on décida d'étendre notre zone d'étude à certains tributaires, on du recourir à une seconde espèce de remplacement, également ubiquiste: le méné émeraude (Notropis atherinoïdes; emerald shiner).

En ce qui concerne la contamination par les substances toxiques organiques, les résultats démontrent clairement que les jeunes de l'année sont de bons indicateurs quantitatifs de substances lipophiles persistantes telles que les BPC, l'HCB et le DDE. Par ailleurs, les concentrations

présentes dans les tissus sont largement au dessus des seuils de détection et surtout bien supérieures aux concentrations retrouvées dans la colonne d'eau. Les résultats portant sur les métaux montrent que les petits poissons reflètent bien les concentrations ambiantes de mercure, qui est probablement présent sous forme méthylée. Par contre, ils semblent être de moins bons indicateurs pour les métaux biologiquement essentiels comme le nickel, le chrome, le zinc et le cuivre. Pour le cadmium et le plomb, les seuils de détection ne sont atteints que lorsque l'on fait face a une contamination importante du milieu. En règle générale, les résultats obtenus pour les métaux semblent plus fiables qu'avec les poissons adultes.

Quelles que soient les espèces considérées, on a pu montrer que la variabilité intra-station était faible pour les produits organiques et pour certains métaux (Zn, Cd, Pb). Par ailleurs, les variations individuelles sont considérablement minimisées par le fait que chaque échantillon est formé de plusieurs dizaines de petits poissons, ce qui est un atout supplémentaire par rapport aux résultats obtenus avec les poissons adultes.

Les variations inter-stations sont significatives, et le patron spatial de répartition de certains contaminants que l'on peut tracer à partir des résultats confirme celui qui a été déterminé par d'autres études utilisant des outils différents. De plus, le caractère régio-spécifique de cette méthode a permis de caractériser des sources ponctuelles jusque-là mal identifiées. Il est encore prématuré de se prononcer sur les tendances temporelles puisque nous ne disposons pas encore de données sur un nombre suffisant d'années.

Signalons finalement que les relations entre les concentrations de certains contaminants retrouvées dans la queue à tache noire et dans la perchaude rendent possible l'élaboration d'un modèle de régression permettant d'extrapoler des concentrations théoriques présentes dans l'espèce cible, à partir de celles rencontrées dans l'espèce de remplacement. Quant aux résultats préliminaires obtenus sur le méné émeraude, ils semblent indiquer une bioaccumulation beaucoup plus importante (5 à 7 fois) que chez les autres espèces étudiées.

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RECHERCHE SUR LA POSSIBLE PRÉSENCE DE MYCOTOXINES PRODUITES PAR LA MYCOFLORE VÉHICULÉE DANS LES SYSTÈMES DE VENTILATION.

Wanda Smoragiewicz, UQAM
Armel Boutard, UQAM
Jeana Neculcea, U. Concordia
Dragos Neculcea, UQAM

Introduction

Les systèmes modernes d'aération des immeubles basés sur la circulation forcée de l'air provoquent depuis un certain temps des problèmes de santé des gens. L'étanchéité des immeubles et l'adoption de mesures d'économie d'énergie restreignent l'apport d'air atmosphérique. Le problème ne se limite pas à l'insuffisance d'air frais. Certains spécialistes indiquent dans les systèmes de ventilation (climatisation, chauffage) des endroits propices à la prolifération des microorganismes. Parmi eux, les mycromycètes nécessitent une attention particulière à cause de leur potentiel toxinogène chez les humains. Le laboratoire de Biotechnologie de l'Environnement de l'UQAM a analysé un certain nombre d'échantillons provenant des systèmes de ventilation de quelques édifices de Montréal et de Québec.

Matériel et méthode

Nous avons reçu les échantillons prélevées à l'aide d'écouvillons. Le travail a été divisé en deux étapes:

1) Analyse microbienne des échantillons.
2) Détection des mycotoxines sécrétées par les souches isolées.

1. **Analyse microbienne des échantillons.**
Nous avons réalisé des dilutions seriées. L'inoculation a été faite par la dispersion de l'inoculum dans le milieu de culture avant la solidification. Nous avons utilisé les milieux de culture spécifiques aux mycochampignons: Sabouraud et pomme de terre - dextrose - agar. Pour les micromycètes cellulosolytiques nous avons utilisé le milieu Czapek à cellulose. Après la croissance des colonies, nous avons effectué le comptage directe et l'identification des souches obtenues.

2. **Détection des mycotoxines sécrétées par les souches isolées.**
Plusieurs souches de Stachybotrys atra et Trichoderma viride, isolées lors de l'étape précédente et reconnues pour leur toxicité ont été transférées dans un milieu nutritif favorable à la synthèse de trichothécènes (riz). Nous les avons maintenues (2 semaines à 26°C et 2 semaines à 10°C) dans des conditions physiques optimales pour la synthèse des mycotoxines. Après la période d'incubation le mycellium et son milieu ont été homogénéisés en solution de méthanol à 90%. Le filtrat de ce homogénat a été soumis aux diverses étapes d'extraction: lavage avec héxane, séparation, complexation avec du gel ferrique. Après filtration le filtrat incolore a été soumis à l'évaporation du méthanol et la solution aqueuse restante a été mélangée avec du dichlorométhane et du Na_2SO_4. La solution finale réduite à quelques gouttes, a été soumise à l'analyse chromatographique en couche mince (TLC) sur des plaques 60TLC à gel de silica. Nous avons utilisé le solvant d'élution éthylacétale-n hexane (5:1). Le développement s'est déroulé en deux étapes avec 4-(p-nitrobenzyl) pyridine (NBP) et tétraéthylène pentamine (TEPA). Les résultats ont été comparés avec le standard - kit trichothécènes.

Discussion et conclusion

Dans les systèmes de ventilation analysés nous avons trouvé les mycromycètes suivants: Penicillum, Aspergillus, Alternaria, Cladosporim, Mucor, Rhizopus, Trichoderma, Poecilomyces, Vlocladium, Gliocladium, Aurobasidium, Acremonium, Chaetomium, Stachybotrys, Epicoccum, Phoma, Fusarium, Curvularia. Parmi ces microorganismes trois genres sont susceptibles de produire des toxines trichothécèns: Trichoderma, Stachybotrys et Fusarium.

Les résultats de chromatographie en couche mince nous indiquent la présence des toxines-trichothécènes - dans le milieu de culture (riz), milieu ensemencé par les souches provenant des systèmes de ventilation précités. Nous avons constaté la coloration bleue sur les chromatogrammes développés, coloration caractéristique des groupements 12, 13 -cpoxy du noyau des trichothécènes.

EVALUATION DE LA CONTAMINATION ET DE LA TOXICITE DES SEDIMENTS DU LAC SAINT-LOUIS (FLEUVE SAINT-LAURENT, QUEBEC)

Louise Champoux[1], Harm Sloterdijk[2], Philippe E. Ross[3,4], Vincent Jarry[4] et Yves Couillard[4]
1: Environnement Illimité inc, 855 boul. de Maisonneuve est, Montréal, Québec, Canada, H2L 1Y8.
2: Environnement Canada, 1001 Pierre Dupuy, Longueuil, Québec, Canada, J4k 1A1.
3: Illinois Natural History Survey, Champaign, Urbana, U.S.A.
4: Dép. de Sciences biologiques, Univ. de Montréal, C.P. 6128, succ. A, Montréal, Québec, H3C3J7.

INTRODUCTION

Le lac Saint-Louis reçoit la plus grande partie de ses eaux des Grands-Lacs et du tronçon international du fleuve Saint-Laurent, régions hautement industrialisées. La dissémination des contaminants a été identifiée comme l'un des problèmes majeurs affectant la qualité de l'environnement du fleuve Saint-Laurent. Une étude réalisée par la Direction des eaux intérieures d'Environnement Canada et le Département de Sciences biologiques de l'Université de Montréal en 1984 et 1985 a évalué la contamination et l'écotoxicologie des sédiments du lac Saint-Louis.

MATERIEL ET METHODES

Des sédiments de surface ont été échantillonnés à environ 60 stations en 1984-1985 et leur contenu en métaux lourds et en contaminants organiques a été analysé, de même que la granulométrie et la minéralogie. La méthode d'élutriation, développée par l'Environmental Protection Agency pour simuler la libération des contaminants des sédiments lors d'un dragage, a été utilisée. Elle consiste à mélanger durant 30 minutes quatre volumes d'eau du lac à un volume de sédiment puis à laisser sédimenter durant une heure. Le surnageant est ensuite centrifugé puis filtré sur membrane de 0,45µm de porosité. Les biotests ont porté sur différents différents trophiques: l'assimilation du ^{14}C par l'algue Selenastrum capricornutum[1], la toxicité aiguë et chronique à l'aide de cladocères (Daphnia pulex, Simocephalus vetulus)[2] et du nématode Panagrellus redividus, l'inhibition de la bioluminescence de la bactérie Photobacterium phosphoreum (test Microtox) et la toxicité aiguë à l'aide du rotifère Brachionus calyciflorus[3].

RESULTATS

Les conditions fluvio-lacustres du lac Saint-Louis sont illustrées par une zone d'érosion et plusieurs zones de sédimentation. Les répartitions spatiales des variables minéralogiques illustrent l'influence des deux affluents du lac (fleuve Saint-Laurent et rivière des Outaouais) sur la composition des sédiments. Les teneurs en contaminants des sédiments sont souvent supérieures aux niveaux recommandés par le Ministère de l'Environnement de l'Ontario pour le dépôt de déchets de dragage en eau libre (Tableau 1). La majorité des contaminants s'accumulent de façon préférentielle dans les zones de sédimentation. La rivière Saint-Louis et la région de Beauharnois contribuent grandement à la contamination du lac, de même que le fleuve, qui fournit entre autres le mirex. Ce dernier est un indicateur du transport à longue distance des contaminants, la seule source connue de mirex étant située au lac Ontario. Les régions les plus contaminées sont le sud de l'île Perrot, l'embouchure de la rivière Saint-Louis et du canal de Beauharnois, le sud des îles de la Paix et la rive nord du lac entre Beaconsfield et la Baie de Valois. Les teneurs retrouvées dans les élutriats indiquent une libération de plusieurs métaux à des niveaux supérieurs aux lignes directrices de qualité de l'eau d'Environnement Canada (Tableau 1). Les corrélations entre les sédiments et les élutriats montrent que les teneurs de certains métaux des élutriats sont reliées à celles des sédiments (Tableau 2). Des effets toxiques ont surtout été observés avec le test Microtox et les algues (Tableau 3). Les résultats des biotests ont montré peu de relations avec les contaminants des sédiments et des élutriats. On a également observé peu de relation entre les résultats des divers tests[4].

CONCLUSION

Les interactions entre les contaminants et les éléments majeurs et nutritifs des sédiments et des élutriats semblent jouer un rôle important dans la réponse des organismes à ces contaminants. Les concentrations de métaux lourds retrouvées dans les élutriats ne reflètent pas leur biodisponibilité. La chimie des élutriats n'est donc pas prédictive du potentiel toxique des sédiments contaminés.

TABLEAU 1. COMPARAISON DE LA CONTAMINATION DES SEDIMENTS ET DES ELUTRIATS AVEC LES CRITERES DE QUALITE DES SEDIMENTS ET LES LIGNES DIRECTRICES DE QUALITE DE L'EAU.

VARIABLES	CRITERES (mg/kg) SEDIMENTS	NB DE STATIONS > CRITERE	LIGNES DIRECTRICES (mg/l)	NB DE STATIONS >LIGNES DIR.
Hg	0,3	32/61	0,0001	6/51
Cu	25,0	31/62	0,002	48/52
Ni	25,0	39/63	0,025	0/52
Pb	50,0	13/63	0,005	16/52
Zn	100,0	49/63	0,05	25/52
Fe	10000,0	54/54	0,30	35/50

TABLEAU 2. CORRELATIONS ENTRE CERTAINS METAUX LOURDS DANS LES SEDIMENTS ET LES ELUTRIATS DU LAC SAINT-LOUIS EN 1984 (N=34; $^{*}p<0,05$;$^{**}P<0,01$; $^{***}p<0,001$; NS $p>0,05$).

Hg	Co	Cu	Ni	Pb	Zn	As	Mn	Fe
0,21 NS	0,08 NS	0,27 *	0,35 **	0,47 ***	0,35 **	0,11 NS	0,60 ***	0,36 **

TABLEAU 3. SYNTHESE DES RESULTATS DES TESTS DE TOXICITE.

	Microtox (EC_{50})	Microtox Inhibition	Algues (inhibition)	Rotifères (survie)	Cladocères (survie)	Cladocères (fécondité)	Nématodes (inhibition)
Nb de réponses	42/50	10/19	13/34	1/16	2/19	2/5	9/45

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DETERMINATION DES CONCENTRATIONS EN PESTICIDES ORGANOCHLORÉS ET BIPHÉNYLES POLYCHLORÉS DANS LES SÉDIMENTS EN SUSPENSION ET L'EAU DU FLEUVE SAINT-LAURENT

André Germain

Environnement Canada, Direction des eaux intérieures (région du Québec), 1001 Pierre Dupuy, Longueuil, Québec.

Un des mandats d'Environnement Canada consiste à mesurer les niveaux des substances toxiques présentes dans l'eau. Ces produits étant généralement présents à des niveaux très faibles, nous avons cherché à en améliorer la détection en utilisant différents moyens. Parmi ceux-ci, l'emploi d'une centrifugeuse à alimentation continue couplée à un échantillonneur d'ea utilisant une résine XAD-2 permet de mesurer les produits associés aux fractions particulaire et dissoute séparément. Nous en avons évalué le fonctionnement en laboratoire avant d'en faire l'emploi en conditions réelles.

Ainsi, l'efficacité de la centrifugeuse à retenir les particules suspension et à respecter l'intégrité du spectre de taille de ces particules a été évaluée à différents débits d'admission d'eau. Pour des teneurs de matières solides dans l'eau inférieures à 10 mg/L, nous avons obtenu des pourcentages de rétention variant de 92% ($\pm$ 3%) pour un débit d'admission d'eau de 0,5 L/min à 81% ($\pm$ 1%) pour un débit de 6,5 L/min. En ce qui concerne le spectre de taille des particules, nous avons observé que l'augmentation du débit d'admission causait une perte importante des solides ayant un diamètre supérieur à 2 um. Nous avons calculé qu'un débit de 4 L/min représente le meilleur compromis entre la capacité de la centrifugeuse à respecter la distribution de taille des particules et la vitesse d'opération qui peut être utilisée en mode opératoire normal.

L'échantillonneur d'eau a été vérifié autant du côté mécanique que chimique. Du côté chimique, nous avons fait des tests de récupération pour les BPC et pour 19 pesticides organochlorés. Nous avons vérifié l'effet de lessivage et du débit de pompage sur la colonne de résine. Nous avons pompé des solutions fortifiées de 10, 18 et 36 L à des débits de 50, 100 et 150 ml/min. La concentration des différents composés chimiques était de 10 ng/L pour chacun. Globalement, il n'y a pas eu d'effet dû au volume pompé ou au débit de pompage sauf pour l'heptachlor, l'aldrine, le pp'-DDE et le B-BHC. Pour l'ensemble des composés organochlorés, nous avons obtenu une récupération de 94% ($\pm$ 19%) et de 80% ($\pm$ 13%) pour les BPC. Du côté mécanique, l'appareil a bien fonctionné. L'écart entre le volume pompé et le volume indiqué par l'appareil a été inférieur à 1% et les intervalles de temps d'échantillonnage ont été respectés.

Après avoir évalué l'efficacité de ces deux appareils en laboratoire, nous avons échantillonné pour les BPC et les organochlorés à 13 stations entre 1984 et 1987. Nous avons ainsi recueilli 23 échantillons formés d'une fraction particulaire et d'une fraction dissoute entre l'extrémité est de Montréal et l'île d'Orléans, près de Québec.

Pour avoir suffisamment de matières solides à soumettre aux analyses, 1000 à 2000L d'eau sont centrifugés à un débit de 4 L/min. Une partie (150 ml/min) de l'eau sortant de la centrifugeuse est aspirée au travers d'une colonne de résine XAD-2 au moyen de l'échantillonneur Seastar. Nous obtenons ainsi un échantillon intégré (50 à 70L) représentatif de la fraction dissoute de la masse d'eau originale. De cette façon, nous avons détecté des niveaux 20 fois plus bas pour les pesticides organochlorés et 40 fois plus bas pour les BPC qu'avec l'échantillonnage traditionnel.

Pour l'ensemble des composés, nous avons obtenu une fréquence de détection de 28% pour les produits associés à la fraction particulaire et de 20% pour ceux associés à la fraction dissoute. En combinant les résultats obtenus dans les deux fractions, des BPC ont été mesurés dans tous les échantillons à des niveaux atteignant 14 ng/L et présentent une teneur moyenne de 2 ng/L. En ce qui concerne les organochlorés, les fréquences de détection pour chacun des composés oscillent de 0 à 95% (moyenne 39%) et les teneurs maximales détectées atteignent 9 ng/L. Lorsque nous comparons ces résultats à ceux obtenus avec l'échantillonnage traditionnel d'un litre d'eau brute, nous observons que les fréquences de détection pour l'ensemble des produits sont différentes (39 vs 13%). En excluant les valeurs des deux isomères du BHC, la fréquence de détection passe de 13 à 5% pour l'échantillon conventionnel alors qu'elle diminue beaucoup moins pour celle obtenue avec la centrifugation, soit de 39 à 36%. De plus, la diversité des produits détectés par les deux techniques depuis 1984 est différente. L'échantillonnage conventionnel à permis de déceler 7 composés sur les 19 analysés (37%) par rapport à 17 sur 20 (85%) pour l'échantillonnage fait au moyen de la centrifugation.

En une occasion, nous avons tenté d'identifier des produits appartenant à la catégorie des polluants prioritaires "base/neutres" dans les fractions dissoutes et particulaires. Nous avons détecté des plastifiants (phtalates) dans les 2 fractions et quelques composés polyaromatiques (PAH), majoritairement associés à la fraction particulaire.

Nous pouvons voir que la technique utilisant la centrifugation nous a permis de mesurer les BPC et les organochlorés à des niveaux inférieurs et à des fréquences de détection plus élevées que la méthode conventionnelle. Elle représente donc un bon outil pour mesurer ces contaminants présents en faible quantité dans l'eau.

Centre de Toxicologie du Québec

Surveillance biologique des travailleurs forestiers manipulant le glyphosate

Jean-Guy Guillot, Dino Manca, Denise Phaneuf,
Onil Samuel et Jean-Philippe Weber

Introduction

La surveillance de l'exposition des travailleurs forestiers aux pesticides qu'ils manipulent n'est pas facile à réaliser. Les méthodes habituelles, utilisées en usine, consistent à mesurer les taux dans l'air ambiant, soit par des stations fixes d'échantillonnage, soit à l'aide de moniteurs personnels qui captent une portion de l'air se trouvant dans la zone respiratoire du travailleur. Les stations fixes ne peuvent évidemment être utilisées à l'extérieur. Les moniteurs personnels, quant à eux, sont difficiles à utiliser dans les conditions de travail qui prévalent en milieu forestier. La représentativité des données qu'ils fournissent peut être mise en doute d'une part parce que l'air échantillonné n'est pas nécessairement l'air respiré par le travailleur et que d'autre part, il peut exister d'autres voies d'absorption importantes du pesticide (cutanée par exemple) dont le moniteur ne peut tenir compte.

Pour tenter d'obtenir un moyen plus fiable d'évaluation de l'exposition des travailleurs exposés au glyphosate, lors d'opérations de débroussaillage par arrosage terrestre, nous avons investigué l'utilisation de la mesure du taux de glyphosate dans l'urine. Cette étude a comporté deux volets: dans un premier temps, nous avons mis au point une méthode analytique permettant de doser le glyphosate urinaire. Par la suite, la méthode a été appliquée à la surveillance d'un groupe de travailleurs forestiers affectés à des opérations d'arrosage de l'herbicide.

Le Centre Hospitalier de l'Université Laval - 2705, boul. Laurier, Québec, Qué. G1V 4G2
TÉL.: (418) 654-2254 (418) 654-2100 (laboratoire)

Mise au point de la méthode analytique

Aucune méthode n'était publiée pour le dosage du glyphosate urinaire. Cependant, à partir des méthodes existantes pour d'autres milieux (eau, sol, fruits), (1, 2), nous avons retenu le principe de la chromatographie ionique suivi de la formation d'un dérivé fluorescent et de sa détection par fluorométrie. Les difficultés analytiques étaient reliées principalement à la composition variable de l'urine qui comprend des concentrations élevées de sels, de molécules organiques à poids moléculaire élevé et des quantités variables de protéines. L'approche retenue consiste à purifier l'urine à l'aide d'une mini colonne d'extraction C 18. Il est ainsi possible de récupérer la totalité du glyphosate dans l'effluent tout en retenant les protéines, pigments ainsi que la majorité des produits acides ou basiques présents dans l'urine. L'extraction subséquente de la fraction recueillie sur ammonium quaternaire permet d'éliminer les interférences résiduelles. Le principal solvant utilisé est l'acide acétique glacial qui permet la neutralisation et l'élution subséquente des acides organiques sans affecter la rétention du glyphosate. La limite de détection obtenue pour le glyphosate dans l'urine est de 30 µg/L (rapport signal/bruit = 3).

Application de la méthode à la surveillance de travailleurs

La méthode a été appliquée à la surveillance d'une équipe d'arrosage comprenant cinq travailleurs: un mélangeur qui avait pour tâche de préparer la solution d'arrosage par dilution du concentré; un opérateur (conduite du tracteur et opération du système d'arrosage); deux signaleurs qui guidaient l'opérateur ainsi qu'un contremaître pour assurer la bonne marche des opérations.

Les travailleurs ont subi un examen médical complet avant le début et après la fin des opérations. Au cours de la période de surveillance (20 journées de travail), nous avons recueilli des échantillons de ces travailleurs à chaque soir et matin.

Par ailleurs, des prélèvements d'air ont été effectués à l'aide de moniteurs personnels par le ministère de l'Énergie et des ressources du Québec, pour fins de comparaisons. (3)

Résultats et interprétations

La répartition des taux urinaires est indiquée au Tableau ci-dessous.

Répartition des taux urinaires de glyphosate selon le travailleur

Travailleur	Nombre d'échantillons	Non-détectable		Déctectable					
				non-quantifiable (A)		quantifiable (B)		Total (A) + (B)	
		N	%	N	%	N	%	N	%
Signaleur 1	36	23	64	13	36	0	0	13	36
Signaleur 2	35	19	54	16	46	0	0	16	46
Opérateur	36	21	58	15	42	0	0	15	42
Mélangeur	33	13	39	6	18	14	42	20	61
Contremaître	38	24	63	12	32	2	5	14	37

Dans le cas du mélangeur, 42% des échantillons contenaient du glyphosate à un niveau quantifiable (> 30 µg/L) et un autre 18% en concentration détectable mais non quantifiable (10-30 µg/L). Les taux chez les autres travailleurs étaient nettement plus faibles.

Nous avons comparé les taux urinaires chez le mélangeur avec les taux mesurés dans l'air ambiant à l'aide de moniteurs personnels. La corrélation est assez mauvaise, ce qui est en général le cas lorsqu'on tente d'établir une relation entre un taux ambiant et un résultat urinaire individuel (4), ces comparaisons s'appliquant mieux à un groupe de travailleurs. Compte tenu des grandes variations journalières, nous avons plutôt estimé l'exposition moyenne, en intégrant les données mesurées au cours de toute la période.

Nous avons ainsi pu démontrer que les taux urinaires mesurés sont compatibles avec les taux calculés à partir des concentrations ambiantes. L'exposition subie par les travailleurs correspond en moyenne à une quantité absorbée d'environ 30 µg par jour avec un maximum de 100 µg/jour. Ces valeurs représentent 0,5% et 1,6% de la dose journalière admissible de 0,1 mg/kg (5).

L'examen et le questionnaire médical n'ont révélé aucune pathologie pouvant être directement attribuée au glyphosage si ce n'est une manifestation d'irritation oculaire chez un travailleur suite à une éclaboussure du produit. Trois travailleurs ont souffert de symptômes de grippe, qui pouvaient s'expliquer par les conditions climatiques (froid et pluvieux) qui prévalaient au cours de la période d'arrosage.

Les résultats obtenus indiquent que la mesure du glyphosate urinaire pourrait s'appliquer à la surveillance de travailleurs exposés à cette substance. Bien que le niveau d'exposition était très faible (< 2% de la DJA), il nous a tout de même été possible de l'apprécier.

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HYDROGEN SULPHIDE TOXICITY

Prior, M.G., Lopez, A., Lillie, L.E., Yong, S.,
and Kelly, W.
Animal Sciences Wing, Alberta Environmental Centre,
Vegreville, Alberta, Canada. T0B 4L0

INTRODUCTION

Hydrogen sulphide occurs naturally in coal, natural gas, oil, and sulphur springs; and is a product of the anaerobic decomposition of sulphur-containing organic matter. It is a by-product of several industries, including desulphurization of sour natural gas; that is, natural gas containing hydrogen sulphide. Many of the natural gas deposits beneath the Province of Alberta contain hydrogen sulphide, which must be removed before the gas may be used (1).

Concerns have been expressed for the potential adverse effects of accidental exposure of human beings, domestic animals and wildlife to hydrogen sulphide as a result of the extraction and processing of sour natural gas and its commercial by-product, sulphur, as well as accidental and uncontrolled emission of sour gas during a "blowout" episode (2).

Several fatalities occur each year as a result of accidental exposure to hydrogen sulphide. The cause of death in fatal exposure has been attributed to paralysis of the respiratory centre. However, autopsy reports of individuals killed in accidental exposures indicate that pulmonary oedema is the single most notable finding (3).

OBJECTIVES

We have investigated the toxicity of hydrogen sulphide with particular emphasis on modelling human health effects. An animal model was established for studying the effects of a single exposure to hydrogen sulphide, namely young, male, Fischer-344 rats exposed to 0, 14, 279 and 558 mg m^{-3} (0, 10, 200 and 400 ppm) hydrogen sulphide.

RESULTS

Histopathological examination showed that lesions in acute, single exposures are largely restricted to the respiratory tract. Inhalation of hydrogen sulphide resulted in severe but reversible necrosis of ciliated nasal epithelium and irreversible necrosis of olfactory epithelium. Lesions in the lung included severe but transitory pulmonary oedema (threshold response) and fibrinocellular alveolitis restricted to the centroacinar region of the lung. Electron microscopy revealed that, except for a reversible blebbing of endothelium from the basal lamina, cells of the air-blood barrier were not structurally affected by hydrogen sulphide. Ciliated epithelial cells were the only component of the lower airways which suffered irreversible toxic injury leading to necrosis. However, necrotic ciliated cells were rapidly replaced by mitosis (4,5).

The most striking lesion in rats exposed to hydrogen sulphide was severe oedema of the lung. This is in agrement with autopsy findings of individuals killed by accidental exposure to hydrogen sulphide. Acute exposure to hydrogen sulphide could therefore, provide a good model for studying the pathogenesis of human pulmonary oedema. Studies are in progress on (1) the significance of necrosis of the olfactory epithelium, since loss or fatigue of the sense of smell is reported in hydrogen sulphide exposures; (2) the effects of long term exposures to low concentrations; and (3) the pathogenesis of pulmonary oedema. Future studies will examine the effects of hydrogen sulphide on reproduction.

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IMPACT ENVIRONNEMENTAL DE L'ÉPANDAGE DE BOUES D'ÉPURATION SUR LES HALDES DE RÉSIDUS D'AMIANTE (1)

On retrouve au Canada d'importants gisements de minerai d'amiante. L'industrie minière qui en découle, affecte une superficie totale de 22.7 km^2 pour l'accumulation des différents dépôts miniers que l'on retrouve sous la forme de montagnes désignées sous le nom de haldes. Celles-ci présentent une forme conique, un sommet aplati, une pente de 35 à 40 degrés et une hauteur d'une centaine de mètres.

Pour la seule région de Thetford Mines, on retrouve 13.5 km^2 de haldes soit presque 60% de tous les rejets d'amiante du Canada. On distingue les haldes de stériles, c'est-à-dire les matériaux enlevés pour atteindre le minerai, des haldes de résidus provenant des usines de traitement qui couvrent une surface de 5.5 km^2 dans la région. Ces dernières sont plus problématiques pour l'environnement, c'est pourquoi nous y avons porté un intérêt particulier.

En plus de leur problème d'ordre esthétique, les haldes de résidus sont soumises à l'érosion et deviennent une source importante de poussières dans l'air et dans l'eau. Sans être une menace d'envergure pour la santé publique, la présence de poussières n'est pas négligeable à cause des risques éventuels. Au sol, ces poussières réduisent la microflore et plus particulièrement à proximité des sites miniers. L'érosion des haldes entraîne dans les cours d'eau des modifications de pH et possiblement certains métaux lourds.

Le recouvrement de certains sites de déchets miniers, par une couverture végétale permanente comme solution à ce double impact esthétique et environnemental causé par l'exploitation minière, a été utilisé avec succès sur une grande variété de déchets miniers (Murray 1977, Sims et Al., 1984). Dans notre cas, des travaux antérieurs (Moore et Zimmerman, 1973 à 1979) montrent qu'il est possible de contrer les conditions hostiles des haldes de résidus: pente abrupte, induration de surface, mauvaise texture, pauvreté extrême en fertilisants, pH de 9, présence de métaux potentiellement phytotoxiques.

Pour réussir à implanter une végétation, il est nécessaire d'utiliser une forte dose d'engrais et d'y ajouter un déchet organique tel le fumier. Étant donné le prix des engrais et la disponibilité insuffisante des fumiers, les boues d'épuration sont devenues une source d'intérêt particulière pour ce type de projet.

Ces boues sont déjà en abondance. On estime, pour le Québec en 1990, une production annuelle de 100 000 tonnes de boues sur une base sèche donc une quantité réelle d'environ 20 fois supérieure sur une base humide. À Thetford Mines, près de 2000 tonnes de boues (18% matière sèche) seront produites annuellement à la station de la Haute-Bécancour récemment construite.

La disposition de ces boues est un problème de première importance dans les coûts d'opération de ce type d'usine à cause de leur volume considérable et des précautions exigées telles l'enfouissement sanitaire ou l'incinération. Les incitations à une telle disposition tiennent au fait que les boues contiennent des métaux lourds, des nitrates, des phosphates, des micro-organismes pathogènes en quantités variables, posant ainsi un risque pour la santé publique et à l'environnement.

Cependant, le contenu des boues en matière fertilisante (azote, phosphore) permet de les substituer en grande partie aux engrais chimiques. En plus, la matière

organique qu'elles apportent, améliore les caractéristiques physiques et microbiologiques du sol. Plusieurs études démontrent le bienfait des boues en agriculture, en foresterie et en restauration des sites dégradés.

Quoique les haldes de résidus ne sont pas à vocation agricole ou commerciale, nous voulons nous assurer que l'épandage des boues sur les haldes se fasse en respectant les normes de qualité de l'environnement. À cette fin, nous avons étudié, à l'aide de parcelles munies de canaux collecteurs, l'effet des boues et des engrais sur la composition des eaux qui infiltrent les résidus d'amiante.

L'alcalinité aiguë des résidus leur confère un grand pouvoir de rétention des phosphates et de la plupart des métaux. Ainsi, aucun élément se retrouve en quantité supérieure aux normes pour les déchets dangereux et même les normes de consommation domestique sont souvent respectées. Parmi les éléments qui dépassent ces dernières normes, sont le cadmium, le magnésium, le nickel, le mercure et le phosphore. Seul, le cadmium et le phosphore semblent être liés à l'application des boues et des engrais.

Au contraire de leur avidité pour les métaux, les résidus sablonneux ne retiennent que très peu l'azote sous forme de nitrate. Avec une fertilisation adéquate, les plantes absorbent la plupart des nitrates produits par la minéralisation des boues. Afin d'éviter la prolifération des coliformes fécaux qui sont une indication de la qualité microbienne des eaux, il suffit d'incorporer les boues aux résidus miniers dans les plus courts délais après leur livraison.

Ainsi le potentiel polluant des boues d'épuration est neutralisé de façon permanente. L'impact des boues sur les plants, sur le sol et les eaux d'infiltration sera présenté. Les taux de boues à utiliser afin de favoriser la prise et la vitalité de la végétation seront fournis tout en indiquant les symptômes de déficience qui peuvent être observés. À partir des analyses foliaires, nous présenterons l'impact positif des boues et la quantité d'éléments lourds que l'on retrouve au niveau des feuilles et du sol.

Nous terminerons en présentant la revégétation des haldes de résidus miniers à l'aide des boues d'épuration comme une perspective concrète à court et moyen terme aux problèmes des sites dégradés de la région de l'amiante et de la disposition des boues d'épuration tout en respectant l'environnement.

(1) D. Lebeuf, H. Lebeuf et L. Brown
Centre spécialisé en technologie minérale
Collège de la région de l'amiante, Thetford Mines

88.02.16

VULPEST, UN NOUVEL OUTIL D'EVALUATION DE LA VULNERABILITE DES EAUX SOUTERRAINES A LA CONTAMINATION PAR LES PESTICIDES

Jean-Pierre Villeneuve, Olivier Banton et Pierre Lafrance
Institut National de la Recherche Scientifique
Université du Québec, INRS-EAU, 2700 rue Einstein
C.P. 7500, Sainte-Foy (Québec) G1V 4C7, Canada

RESUME

Le modèle VULPEST est un outil d'évaluation de la vulnérabilité des eaux souterraines à la contamination par les pesticides. Il permet de quantifier le risque de pénétration du contaminant, en évaluant la quantité de pesticide pouvant parvenir à la nappe. En utilisant les distributions des paramètres d'entrée représentant leur variabilité spatiale et temporelle, il fournit un résultat de type statistique. Ce résultat peut être interprété en niveau de vulnérabilité par comparaison à des normes. Cette démarche permet de quantifier la vulnérabilité d'une nappe à un pesticide donné. Ceci permet d'orienter les aspects règlementaires et techniques de l'utilisation des pesticides. Enfin, sa simplicité d'utilisation, sa rapidité d'exécution, et la disponibilité habituelle des données requises en font un outil accessible à des gestionnaires compétents mais non nécessairement spécialistes.

CONTEXTE

Le problème de la contamination des eaux souterraines par les pesticides est relativement nouveau et de plus en plus préoccupant. Ceci découle d'une utilisation croissante des pesticides (surfaces et doses d'application), de leur grande toxicité, de leur persistance et de leur accumulation dans le système. L'épandage des pesticides peut constituer sous certaines conditions un problème de contamination diffuse. La qualité de l'eau souterraine peut être plus ou moins altérée par cette source de contamination non-ponctuelle, suivant la nature du sol, du sous-sol et le type de pesticide. Ces caractéristiques conditionnent la vulnérabilité des eaux souterraines à la contamination.

LE MODELE VULPEST

L'outil que nous avons développé est destiné à l'évaluation des risques de contamination de l'eau souterraine par les pesticides. Dans notre démarche, la vulnérabilité est définie comme toute pénétration de contaminant dans le système d'eau souterraine (nappe aquifère). L'évaluation de la vulnérabilité dans ce contexte repose sur l'évaluation des quantités de pesticides susceptibles de parvenir à la nappe. Cette approche prédictive s'appuie sur la modélisation des phénomènes régissant le transport et le devenir du contaminant dans la zone insaturée du sol. Les principaux phénomènes que l'on modélise sont le transport du pesticide (lié au déplacement de l'eau), le retard dans ce transport (lié à l'adsorption), et la persistance du pesticide (liée à se dégradabilité).

Compte tenu du caractère diffus de la contamination, de la variabilité spatiale des valeurs des différents paramètres et des incertitudes dont

elles sont entachées, nous avons adopté une démarche de type Monte-Carlo. Cette démarche consiste à effectuer un nombre suffisant de simulations pour que l'ensemble des résultats qui en résultent soit représentatif de la variabilité des paramètres. Ainsi, pour chaque simulation, les paramètres utilisés par le modèle sont fixés par tirage aléatoire à partir des distributions de ces paramètres. L'intérêt de cette approche est qu'elle intègre la variabilité spatiale des processus et qu'elle fournit des résultats interprétables sur une base statistique.

CONCLUSION

Le modèle qui a pour but de prédire la quantité de pesticide qui parvient à la nappe, a été établi en prenant en considération les principaux processus qui régissent le cheminement et le destin des pesticides dans la zone non saturée. Il est conçu pour être utilisé notamment par des gestionnaires. En ce sens, il est un outil pratique pour l'utilisateur qui peut aisément visualiser les données entrées et les sorties.

L'application du logiciel VULPEST sur deux sites québécois (région de Portneuf (aldicarbe) et station agronomique de St-Augustin (atrazine)) a permis de montrer l'intérêt d'un tel outil dans l'évaluation de la vulnérabilité des eaux souterraines de la nappe. Il a en effet été possible de quantifier les risques de contamination de l'eau souterraine liés à l'utilisation d'un pesticide avec des grandeurs physiques significatives. Ce sont des grandeurs qui peuvent être réellement mesurées sur des échantillons d'eau, et qui peuvent être directement comparées à des normes, des critères ou des seuils de qualité.

Le modèle VULPEST apparait donc comme un outil précieux d'aide à la décision pour ceux qui doivent régir l'utilisation des pesticides et ceux qui se préoccupent de la conservation de la qualité des ressources en eaux souterraines. A partir des normes et seuils fixés par l'utilisateur, le modèle détermine le niveau de vulnérabilité du système.

REMERCIEMENTS

Les travaux sur la contamination des eaux souterraines réalisés à l'INRS-Eau ont pu être effectués grâce aux subventions de la Division du Contrôle des Contaminants du Ministère de l'Environnement du Canada et de la Fondation Donner.

CONTAMINATION DU LAC SAINT-PIERRE PAR CERTAINS POLLUANTS ORGANIQUES ET INORGANIQUES

C. Langlois, J. Bureau et H. Sloterdijk

Environnement Canada, Direction des eaux intérieures, 1001 Pierre Dupuy, Longueuil, Qc, J4K 1A1.

Le bassin de drainage du lac Saint-Pierre inclut la région métropolitaine de Montréal et la région internationale des Grands Lacs. Il reçoit directement les eaux provenant de quatre tributaires importants du fleuve Saint-Laurent, les rivières Richelieu, Yamaska, Saint-François et Nicolet. La Direction des Eaux Intérieures (Région du Québec) a amorcé au cours de l'année 1986, en collaboration avec l'Institut National de Recherche en Eau et le Ministère de l'Environnement du Québec, une étude sur la présence et le cheminement des substances toxiques dans ce tronçon du fleuve.

L'échantillonnage et les analyses chimiques ont porté sur l'eau, les sédiments et les poissons. Les échantillons d'eau ont été récoltés pour 26 stations selon la méthode conventionnelle (1 L d'eau brute) et pour 6 stations (entrée et sortie du lac) à l'aide d'une colonne de résine XAD-2 qui retient les produits organochlorés présents dans 70 L d'eau préalablement centrifugée. Les sédiments en suspension ont été récoltés aux mêmes 6 stations par centrifugation de 2000 L d'eau. Les sédiments de fond ont été recoltés à 37 stations (lac et delta de Sorel) à l'aide d'une benne Eckman (30 cm X 30 cm). Les poissons juvéniles (Queue à tache noire et Perchaude d'âge 0 +) ont été capturés à 13 stations (lac et tributaires) à l'aide de seines alors que les poissons adultes (Grand brochet, Doré jaune, Barbotte brune, Perchaude, Meunier noir, Poisson-castor et Lotte) ont été capturés à 6 stations (lac et delta de Sorel) à l'aide de verveux. Des analyses chimiques ont été effectuées pour les métaux, les pesticides organochlorés et les biphényles polychlorés. Dans le cas des poissons, ce sont des homogénats d'invidivus entiers (juvéniles) et des homogénats de chairs ou d'individus entiers (adultes) qui ont été analysés.

Dans les eaux de surface, les concentrations de BPC dépassent fréquemment la valeur recommandée par le Conseil Canadien des Ministres des Ressources et de l'Environnement (CCMRE) pour la protection de la vie aquatique d'eau douce (1 ng/L); dans l'eau brute, la fréquence de détection pour les BPC est de 20% alors qu'elle atteint 66% dans l'eau centrifugée. Les deux isomères de l'hexachlorocyclohexane (alpha- et gamma-BHC) sont détectés dans environ 80% des échantillons, mais les concentrations sont toujours inférieures à celles recommandées par le CCMRE (10 ng/L de BHC total). Plusieurs autres pesticides organochlorés ont été détectés dans l'eau centrifugée, incluant le chlordane, l'hexachlorobenzène, l'endosulfan, l'endrine, la dieldrine et les différentes formes de DDT (DDD, DDE et DDT).

Dans les sédiments, les BPC sont présents dans tous les échantillons de sédiments de fond et de sédiments en suspension. Les concentrations dans les sédiments de fond atteignent un maximum de 310 uk/kg à une station du delta de Sorel. La concentration moyenne de BPC

obtenue en amont du lac (Lanoraie: 110 ug/kg) dans les sédiments en suspension est significativement différente de celle obtenue en aval (Trois-Rivières: 40 ug/kg). De plus, seuls les BPC ont été détectés en aval alors que plusieurs pesticides organochlorés ont été détectés en amont, dont l'hexachlorobenzène, l'alpha-BHC, le chlordane et les différentes formes de DDT. Le DDE est présent dans presque 100% des échantillons de sédiments de fond et les teneurs moyennes de BPC, DDE et mercure sont significativement plus élevées dans le delta de Sorel que dans les autres secteurs du lac (excluant le secteur sud, occupé par le Ministère de la Défense Nationale, pour lequel aucune donnée n'est présentement disponible).

Dans les poissons, les contaminants organochlorés les plus fréquemment détectés sont le DDT (surtout sous la forme DDE) et les BPC. Dans les chairs, les teneurs de ces deux composés sont toujours inférieures aux normes fédérales de mise en marché (DDT: 5 mg/kg; BPC: 2 mg/kg), mais elles sont 10 à 20 fois plus élevées dans les poissons entiers, dépassant parfois la norme précitée pour les BPC chez le Doré jaune et le Meunier noir. Autant chez les poissons juvéniles que chez les poissons adultes, c'est dans le delta de Sorel que les teneurs moyennes de BPC et DDT sont les plus élevées (BPC/chairs: 66 ug/kg, entiers: 1150 ug/kg, juvéniles: 167 ug/kg; DDT/chairs: 8,2 ug/kg, entiers: 102,8 ug/kg, juvéniles: 8,3 ug/kg). Ce sont le Doré jaune et la Barbotte brune qui affichent les plus fortes concentrations de BPC et DDT dans leurs chairs (respectivement 83 et 75 ug/kg pour le BPC, 9,9 et 10,5 ug/kg pour le DDT). Le chlordane a été détecté dans 61% des échantillons de poissons entiers et l'hexachlorobenzène dans 49% des échantillons de poissons juvéniles. Le mirex n'a été détecté que chez quelques échantillons de Doré jaune et Barbotte brune. Dans le cas du mercure, les teneurs dans les chairs de 75% des gros spécimens de Grand brochet ($>$ 70cm) et de Doré jaune ($>$ 50cm) excèdent la norme fédérale de 0,5 mg/kg.

En conclusion, les résultats obtenus montrent que les contaminants majeurs dans le lac Saint-Pierre sont les BPC, le DDT et le mercure. La répartition spatiale des concentrations de BPC et de DDT suggère par ailleurs que les contaminants provenant de l'amont sont déposés et/ou bioaccumulés en grande partie dans le delta de Sorel et dans le lac. La concentration moyenne en BPC dans les sédiments de fond du lac Saint-Pierre (112 ug/kg) est plus élevée que celle du lac Saint-Louis ($<$ 90 ug/kg), mais elle reste inférieure à celle du lac Saint-François (médiane de 170 ug/kg). La contamination des poissons est par ailleurs comparable à celle observée dans les autres tronçons du fleuve Saint-Laurent (incluant les lacs Saint-Louis et Saint-François), sauf en ce qui concerne le mercure dont les teneurs sont plus élevées dans les poissons du bassin de la rivière des Outaouais, du lac des Deux-Montagnes et du sud du lac Saint-Louis.